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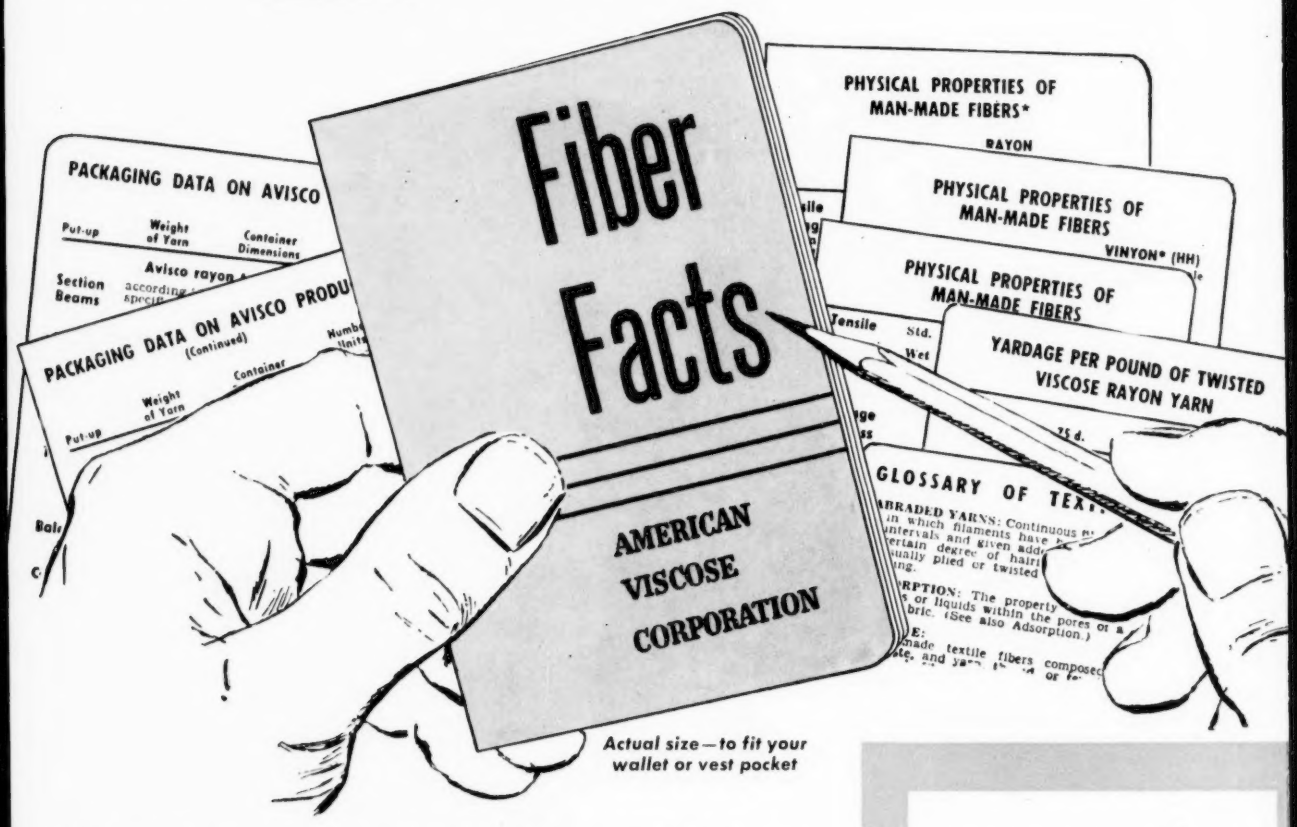

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TEXTILE RESEARCH JOURNAL

VOL. XXIII, No. 7 July, 1953

The Reaction of Formaldehyde and Phenols with Wool

Part I: The Linking of Phenols

Kenneth G. Johnson*

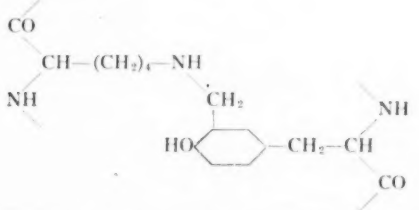
Research Department, Wolsey Limited, Leicester, England

Abstract

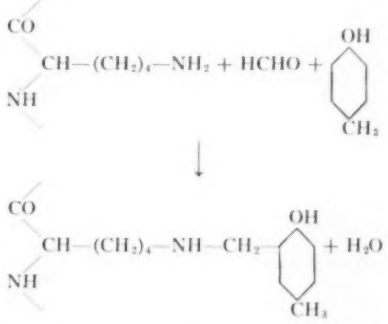
The reaction of wool keratin with formaldehyde and phenols in dilute solution and at neutrality is discussed. A covalent linking of the phenol to the free amino groups of the keratin under such conditions that the reactants do not condense and polymerize is suggested.

Introduction

Reactions of proteins with formaldehyde involving the amino and phenolic groups have been described by Fraenkel-Conrat and Olcott [4]. They showed that stable cross-links are formed from the primary addition product of formaldehyde and amino groups —methylolamines—by condensation with the reactive CH groups on the phenol rings. This is a typical Mannich reaction [3], and has been shown to occur in wool keratin by Alexander, Carter, and Johnson [2]. Cross-links are formed between the ε-amino groups of lysine and the 3-position in the phenol radical of tyrosine:



By treating certain proteins with a solution of formaldehyde and a phenol, Fraenkel-Conrat *et al.* demonstrated that this reaction can be used to introduce phenols into a protein that is rich in amino groups:



They found the ideal reaction conditions to be a neutral or slightly acid solution at about 40°C, although a somewhat slower reaction proceeds at room temperature. The formaldehyde and phenol will react with amino groups, but not with guanidyl or amide groups.

Initial experiments showed that this reaction proceeds in wool keratin under mild conditions. A

* Present address: County Perfumery Co. Ltd., Stanmore, Middlesex, England.

study of the nature of the reaction forms the subject of this paper.

Experimental Methods

Materials

A completely extracted Merino wool fabric was used, knitted from a twofold 18's yarn of 56/58s quality using 12 needles and 18 courses per inch. The only previous treatment the wool received was scouring in dilute soap and ammonia to remove dirt and wool grease.

Application of Formaldehyde and Phenols to Wool

Commercial 40% formalin solution was used for all treatments, the formic acid and methyl alcohol present in the solution having no effect on the results. In the case of water-soluble phenols, the wool was first wetted in a 1% Dispersol V.L. (I.C.I.) solution, and then treated in a solution of the phenol and formaldehyde at a liquor-to-wool ratio of 30:1, unless otherwise stated, washed in running water for 24 hrs., and dried at 110°C. Where weight increases were to be determined, the wool was previously dried to constant weight at 110°C, weighed, and then finally dried to constant weight at 110°C. The application of sparingly soluble phenols was from aqueous alcohol.

Tests of Fastness

Soap washing.—The treated fabric was stirred gently in a 1% soap solution at 70°C for 30 min., at a liquor-to-wool ratio of 50:1.

Acid.—The treated fabric was boiled for 30 min. in $N/100$ HCl, at a liquor-to-wool ratio of 50:1.

Solvents.—The treated fabric was extracted by refluxing in a Soxhlet for 2 hrs.

Estimation of Polymer Formation

The extent of polymerization in the liquor was measured by the loss of free formaldehyde in solution. The formaldehyde and phenol were heated together in a flask under reflux either in aqueous or aqueous alcoholic solution. The free formaldehyde was estimated before and after 30 and 60 min. by the sulfite method [5]. Five milliliters of the liquor was removed, made just alkaline to thymolphthalein, which is the preferred indicator [6], and neutralized with $N/10$ HCl. Twenty milliliters of M Na_2SO_3, also neutralized to thymolphthalein with HCl, was added, and the whole was titrated with $N/10$ HCl.

Microscopic Examination of Fibers

A slide prepared from the fibers under test was studied in two directions at right angles. One hundred fibers were counted in each direction, and the percentages of unmodified and modified fibers were calculated. If the scales resemble those of a perfect untreated fiber, the fiber is classified as "unmodified," but if any stripping or masking of the scales is visible, the fiber is "modified." Photomicrographs were taken of fibers that were considered to be representative of all those examined. The photomicro-

TABLE I. PHENOLS LINKED TO WOOL BY FORMALDEHYDE AND THEIR FASTNESS

Treatment	Over-all weight increase (%)				
	Initial	After fastness test in: Soap	Acid	Ether	Alcohol
Phenol	1.1	−0.6	0.2	0.1	−0.3
Phenol+HCHO	4.6	3.9	nil	3.6	3.9
o-Cresol	2.9	0.6	0.5	0.4	−0.2
o-Cresol+HCHO	2.8	1.1	−0.4	1.0	0.8
m-Cresol	5.8	0.4	0.1	0.1	0.4
m-Cresol+HCHO	15.7	14.5	0.2	10.1	10.4
p-Cresol	7.7	2.2	−0.1	0.6	−0.4
p-Cresol+HCHO	4.9	2.1	−0.9	2.4	2.0
Resorcinol	0.4	0.1	−0.4	−0.1	−1.0
Resorcinol+HCHO	3.0	3.0	0.2	2.9	3.0
β-Naphthol	0.2	nil	−0.4	nil	0.1
β-Naphthol+HCHO	5.9	5.3	1.0	5.4	5.1
α-Naphthol	0.9	0.2	0.1	−0.6	−0.2
α-Naphthol+HCHO	16.0	16.0	15.0	15.4	15.8
Phloroglucinol	0.5	0.2	−0.8	0.1	−0.4
Phloroglucinol+HCHO	4.51	4.51	4.13	4.50	4.48
2,6-Dimethylol-*p*-cresol	−0.21	—	—	—	—
2,6-Dimethylol-*p*-cresol+HCHO	−0.24	—	—	—	—

TABLE II. EFFECT OF CONCENTRATION ON WEIGHT INCREASE

Concentration (M)	Weight increase (%)
0.006	0.27; 0.29
0.013	1.01; 0.95
0.033	2.10; 2.02
0.133	3.18; 3.31
0.333	4.80; 4.78
0.667	4.82; 4.85

graphs are shown at a magnification of approximately 500 ×.

Results

The chemical linking of phenols into proteins by reaction with formaldehyde at the free amino groups has been demonstrated by Fraenkel-Conrat and Olcott [4] and discussed in the Introduction. They showed that the covalent links formed are stable to alkaline hydrolysis but are broken by hot acids with liberation of the phenol.

The reaction of nine different phenols and wool keratin with or without formaldehyde has been studied by means of the weight increases obtained. The fastness to soap, acid, and solvents has also been examined. These results are shown in Table I.

Having established that many phenols may be linked to wool in a manner fast to alkaline washing or solvent extraction, a detailed study of the weight increases obtained under varying conditions was made using a suitable phenol. Resorcinol was the phenol chosen, because it is readily soluble in water and gives a convenient weight increase. It was found that there is no significant change in weight on stirring wool in water alone under all of the experimental conditions used except those with alkaline pH buffers. Wool stirred for 30 min. at 60°C in pH 10 buffer showed a 0.84% loss in weight, and in pH 12 buffer a 1.37% loss; corrections were made for these losses.

Variation of Concentration

The wool was treated at 60°C for 30 min. at neutrality, the concentrations of both resorcinol and formaldehyde being kept equal (Table II).

Table III shows the effect of varying only the formaldehyde concentration, the resorcinol concentration being kept at 0.667M.

Table IV shows the effect of varying only the resorcinol concentration, the formaldehyde concentration being 0.667M throughout.

It is seen that if the treatment is carried out at 60°C for 30 min., there is a limiting weight increase of 4.8%–5%.

Variation of Temperature

The wool was treated in a solution 0.067M with respect to both resorcinol and formaldehyde for 30 min. at neutrality. Table V shows the effect of varying the temperature.

There appeared to be a small degree of polymerization taking place in the bath at 100°C.

TABLE III. EFFECT OF FORMALDEHYDE CONCENTRATION

HCHO concentration (M)	Weight increase (%)
0.0067	1.99; 1.90
0.013	2.18; 2.02
0.033	2.98; 3.07
0.133	3.15; 3.60
0.333	4.80; 4.81
0.667	4.93; 4.84

TABLE IV. EFFECT OF RESORCINOL CONCENTRATION

Resorcinol concentration (M)	Weight increase (%)
0.0067	0.26; 0.41
0.013	0.88; 1.01
0.033	1.75; 1.75
0.133	3.58; 3.46
0.333	4.70; 4.80
0.667	5.05; 4.91

TABLE V. EFFECT OF TEMPERATURE

Temperature (°C)	Weight change (%)
0	−0.51; −0.60
20	zero ; −0.07
40	+0.12; +0.26
60	+1.86; +2.01
80	+3.28; +3.34
100	+6.00; +6.17

TABLE VI. EFFECT OF TIME OF TREATMENT

Time (min.)	Weight increase (%)
5	0.33; 0.21
10	0.74; 0.66
15	0.87; 1.02
30	1.78; 1.91
60	2.75; 2.66
240	4.38; 4.50

TABLE VII. EFFECT OF pH OF LIQUOR

pH	Weight change (%)
2.10	+0.13 ; −0.02
3.92	+0.84 ; +0.94
6.10	+1.34 ; +1.60
7.99	+3.04 ; +3.08
9.70	+0.99*; +0.64*
11.8	−0.60*; −0.77*

* Corrected for the effect of alkaline solution on wool.

TABLE VIII. LOSS OF FREE FORMALDEHYDE BY POLYMERIZATION

Phenol	Titer Initial	Titer 30 min.	Titer 60 min.	Loss of HCHO (%)
Phenol	11.6	11.0	10.5	9.5
Resorcinol	11.7	11.8	11.1	5.1
β-Naphthol	11.4	10.9	10.9	4.4
α-Naphthol	11.5	10.4	8.2	28.7

Variation of Time

The wool was treated in a solution 0.067*M* with respect to both resorcinol and formaldehyde at 60°C and neutrality. Table VI shows the effect of varying the time of treatment.

Variation of pH

The wool was treated for 30 min. at 60°C in a 0.067*M* solution of resorcinol and formaldehyde. Table VII shows the effect of varying the pH of the liquor.

Estimation of Polymer Formation

The titration figures and over-all loss of formaldehyde from several phenol-formaldehyde baths are recorded in Table VIII. The liquors all correspond to the strongest which would be used for wool treatment—*i.e.*, 0.333*M* with respect to both the phenol and formaldehyde. The treatment was for 30 min. at 60°C and neutrality (no buffer).

Microscopic Examination of Fibers

The results of the microscopic examination of the fibers taken from fabrics treated as in Table I are given in Table IX.

Typical fibers taken from untreated and treated fabrics are illustrated in Figure 1 and Figures 2–4, respectively.

Discussion

It was found that the reaction described by Fraenkel-Conrat and Olcott [4] proceeds quite

FIG. 1. *Untreated wool fibers.*

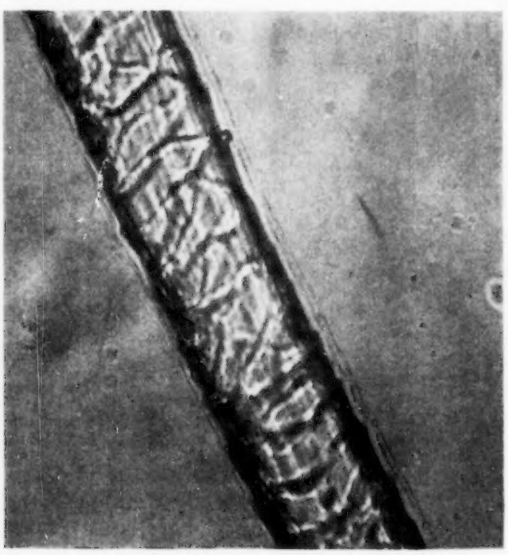


FIG. 2. *Wool fibers treated with formaldehyde + phenol.*

TABLE IX. MICROSCOPIC EXAMINATION OF FIBERS

Treatment	Unmodified (%)	Modified (%)
None	89	11
Phenol+HCHO	86	14
o-Cresol+HCHO	90	10
m-Cresol+HCHO	90	10
p-Cresol+HCHO	86	14
Resorcinol+HCHO	87	13
β-Naphthol+HCHO	86	14
α-Naphthol+HCHO	4	96
Phloroglucinol+HCHO	88	12
2,6-Dimethylol-*p*-cresol+HCHO	89	11

readily with wool keratin. Many phenols were employed, and in all cases it was found that reaction with formaldehyde and the phenol gives a greater weight increase than treating with the phenol alone. With the exception of α-naphthol, it was found that the phenolic linkage is broken by hot acid, with removal of the phenol, but is stable to hot alkaline solutions and solvents, even though the phenols are very soluble in alkalies and solvents; these findings substantiate the reaction proposed by Fraenkel-Conrat and Olcott. In the case of α-naphthol there appeared to be some polymerization taking place in the liquor. Furthermore, the treated fibers showed considerable scale masking (Table IX and Figure 4), and masses of solids were evident on the fiber. This is typical of one type of polymer deposition, as shown by Alexander [1] in the case of wool treated with urea-formaldehyde resins or methylsilicon trichloride. The fibers subjected to the other treatments described did not have this appearance (Figures 2 and 3), and the percentage of unmodified fibers was found to be the same as for untreated wool (Table IX). The formaldehyde + α-naphthol bath lost formaldehyde to the extent of nearly 30% of the original (Table VIII). It seems highly probable, therefore, that the high weight increase, stable to acid hydrolysis, which is obtained in the case of α-naphthol is due to deposition of polymer on the fibers. In all other cases it has been shown that the conditions and concentrations employed were such that phenol-formaldehyde condensation products and their polymers were not formed and the fibers retained their original appearance.

A detailed study of the formaldehyde and resorcinol reaction has been made, and it would appear that the optimum conditions of treatment are a concentration of 0.133*M* with respect to both formaldehyde and resorcinol at 60°C for 30 min. The optimum pH is between 7 and 8, but experiments conducted without buffers give good results. This treatment with formaldehyde and resorcinol gives

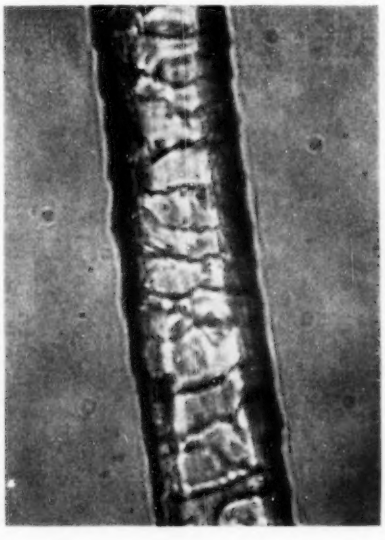
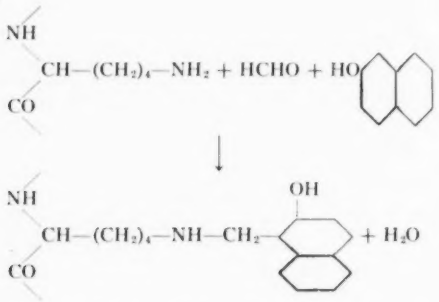


FIG. 3. *Wool fibers treated with formaldehyde + β-naphthol.*

FIG. 4. *Wool fibers treated with formaldehyde + α-naphthol.*

a weight increase of approximately 3.5%. As the concentration of the reactants is increased, the reaction reaches a limiting value at a weight increase of 4.8% to 5.1%. Only one treatment exceeded this value—that at 100°C, when polymerization was evident in the liquor.

These optimum conditions found for the formaldehyde-phenol reaction are very similar to those found by Alexander, Carter, and Johnson [2] for the formation of lysine-tyrosine cross-links in wool keratin with formaldehyde. They found that treatment with 0.15*M* formaldehyde solution at 60°C for 30 min. at neutrality gave the best results. This supports the theory that the phenols are linked through a methylene bridge to the ε-amino groups of lysine:



2,6-Dimethylol-*p*-cresol, in which the reactive groups have been blocked by previous reaction with formaldehyde, does not react with wool keratin and formaldehyde, which also supports this proposed linkage.

Summary

It has been shown that reactions of phenols and formaldehyde with wool keratin give greater weight increases than the corresponding reactions with the phenols alone, and that this is not due to the deposition of polymers.

This weight increase is stable to subsequent alkaline hyldrolysis or extraction with organic solvents, but is readily removed by warm acid hydrolysis.

The optimum conditions for the reaction are very similar to those required for producing methylene cross-links between lysine and tyrosine residues in wool keratin.

It seems probable that the phenols are covalently linked by methylene bridges to the ε-amino groups of lysine.

Acknowledgment

The author wishes to thank Messrs. Wolsey Limited, Leicester, England, for permission to publish this work.

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(Manuscript received March 4, 1953.)

Part II: The Formation of Covalent Linked Mothproofing Agents

Abstract

A brief review is made of the known methods of mothproofing wool, with particular reference to the fastness obtained by each method. The treatment of wool with formaldehyde and certain phenols, especially halogen-substituted phenols, is studied and shown to give good resistance to attack by clothes moth larvae in many cases. The fastness obtained by this treatment is also investigated, and a mechanism is suggested.

Introduction

The mothproofing of wool entails a treatment to impart resistance to the attack of the keratin-digesting larvae of certain moths or beetles. The most common of these is the common clothes moth, *Tineola bisselliella*, which is used for all the mothproofing tests in the present study. Many methods of testing the mothproofing of wool have been evolved [2, 10, 18, 29], but the one chosen for this study is that in general use at the Wool Industries Research Association, Leeds, England, and described by Hartley, Elsworth, and Barritt [17]. This is essentially based on the methods of Burgess [6, 7] and Stiteler [33].

Methods of Mothproofing Wool

Certain dyes have been reported to impart some mothproofing to wool, the main ones being 2,4-dinitro-α-naphthol (Martius Yellow) by Meckbach [27] and 3,5-dinitro-*o*-cresol by Hartley, Elsworth, and Barritt [17]. In 1928 the use of colorless dyes began with the development of the Eulans [35, 36]. They were condensation products of aldehydes and chlorophenols, giving di- or triphenylmethane derivatives containing both chloro and hydroxy substituents. These products gave only moderate resistance to larval attack, and their fastness to warm alkaline washing was poor. They were followed by Eulan N, CN, and CN Extra, which Clark [8] reported to be the sodium salts of sulfonated triphenylmethane derivatives containing chloro and hydroxy groups. These compounds impart a good resistance and are fast to all normal processing, but are rather expensive to use. Another series of colorless mothproofing dyes are the sodium salts of haloacylamino sulfonic acids of the aromatic series [25]. A very important member of this group is Mittin FF, which is easily applied from a dye bath and is fast to all normal processing. Läuger, Martin, and Müller [21] described it as a substituted urea in which the substituents are dichlorophenyl and diphenyl ether, itself chlorinated and containing a sulfonic acid group to give water solubility.

Many compounds containing fluorine have been used to impart resistance to larval attack. Simple inorganic fluorides [3, 4, 20, 24, 34] give a good resistance owing to their fluorine content, but are readily washed out by water. An organic fluorine compound has recently been marketed by Bocan Chemical Corp., which claims it to give good fastness to washing. According to Moncrieff [28], this may be 1,6-diamino-2,2′-difluorohexane.

Several organic halogen compounds have been used as mothproofing agents, including pentachlorophenol (Mystox) and *p,p′*-dichlorodiphenyltrichlorethane [30], but these compounds have no affinity for wool and are readily washed out by alkaline solutions or they volatilize. Their use is limited to a solvent application during dry-cleaning.

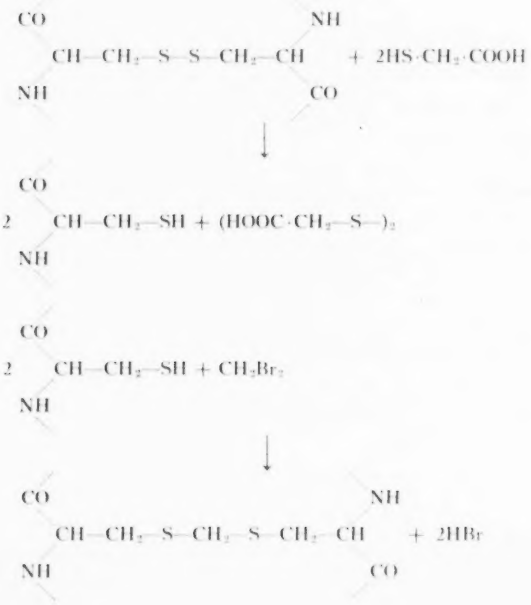
Halogen-substituted quaternary phosphonium bases have been used [23] with limited success.

Resistance to attack by clothes moths after treatment of wool with epichlorhydrin was reported in a B.I.O.S. Technical Report [5]. The wool was treated at 50°C in the vapor of epichlorhydrin without a catalyst. This process was examined in our laboratory and good mothproofing was obtained. According to Fraenkel-Conrat [11], 1,2-epoxides react with wool both by esterification of the carboxyl groups and by reaction with the free amino groups.

A method of mothproofing wool by treatment in a 1.0%–1.5% solution of formaldehyde at 35°C for 20 hrs. at a pH less than 1 was described by McLean and Traill [26]. The optimum pH is 0–0.5 and the acid must be sulfuric or hydrochloric; sodium sulfate or sodium chloride may also be present. The wool is finally washed well in cold water to remove excess formaldehyde and then dyed or, if dyeing is not required, the wool is neutralized with sodium car-

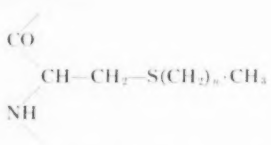
bonate at room temperature. A good resistance to larval attack is afforded by the process, but it is not fast to washing. The main disadvantages to the process are the very harsh handle of the treated wool, a tendency to yellow if hydrochloric acid is used, and the long time required for the treatment. No theory is given for the manner in which the wool is rendered mothproof, but since the effect will not stand a normal soap washing, any modification of the wool structure seems very improbable. The resistance is very likely due to loosely absorbed formaldehyde, perhaps reversibly held as methylolamines.

Geiger, Kobayashi, and Harris [13] showed that it is possible to render wool more resistant to attack by enzymes and chemical reagents by conversion of the disulfide linkages to *bis*-thioether linkages. They also showed that wool modified in this way is more resistant to larval attack, a fact which might be expected from the findings of Linderstrøm-Lang and Duspiva [22]. The cystine linkages are first reduced to thiol groups by treatment with calcium thioglycollate at pH 5 and 50°C for 2 hrs. The reduced wool is washed and then relinked by treatment with an alkylene dihalide—*e.g.*, methylene dibromide—at pH 8 and 50°C for 2 hrs. Approximately 0.0005 mol of alkylating agent per gram of wool is necessary for relinking. The two stages of the reaction are as follows:

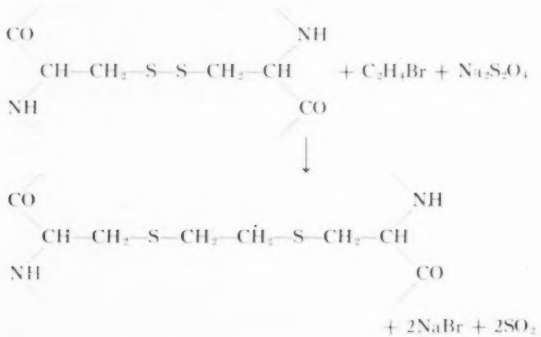


Besides methylene dibromide, trimethylene dibromide, tetramethylene dibromide, and 1,4-dichlorobutene-2 are described as very good alkylating agents for the second reaction, but ethylene dibromide is unsatisfactory. A series of wools with gradually diminishing cystine contents, obtained by the formation of new linkages, was examined for resistance to attack by moth larvae and the black carpet beetle. From these, Geiger, Kobayashi, and Harris suggested that reduction of the cystine content of wool to 6% gives as much protection as more extensive treatments, and pointed out that the mothproofing obtained is not affected by dry-cleaning or washing because it is "built into" the molecule as an integral part of its chemical structure. Their mothproofing results have been confirmed by Hartley, Elsworth, and Barritt [17], who also found that methylene iodide and ethylene dichloride are ineffective alkylating agents; judging from the thiol and cystine sulfur contents of the reduced and alkylated wool, as indicated by the Shinohara technique [31, 32], the required reduction in disulfide links is not obtained.

Harris and Patterson [15] described the use of monohalides as well as dihalides, the final product being a monothioether:



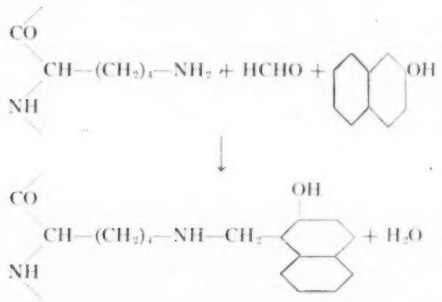
More recently, Harris and Brown [14] described a one-stage method of converting the disulfide linkages into *bis*-thioether linkages. They used a 4% aqueous solution of sodium hydrosulfite containing ethylene dibromide as an emulsion at 50°–85°C and pH 8 for 30 min. The reaction is as follows:



Harris and Brown stated that mothproofing tests have not been carried out on wool treated in this manner, but there is every expectation that a satisfactory mothproof will be obtained.

This method of mothproofing depends upon modifying the molecular structure of the wool keratin in such a manner as to render it indigestible to the larvae. All of the other methods depend upon the introduction of toxic substances held to the fibers either by simple absorption or ionic charges. Apart from two nitrophenols and formaldehyde, these toxic compounds all contain halogens, and some of them have phenolic groups in addition. It can readily be appreciated that any method of covalently linking toxic compounds into the molecular structure of wool keratin will give a permanent resistance to the attack of larvae in the same manner as the modification of the disulfide link.

In Part I of this work [19] it was shown that phenols can be linked convalently to wool keratin by means of a methylene bridge employing formaldehyde as the linking agent:



The optimum reaction conditions for this linking are 60°C for 30 min. at neutrality, using a solution 0.133*M* with respect to both formaldehyde and phenol. The link formed is stable to hot alkalies and organic solvents, but is broken by hot acidic solutions, with liberation of the phenol.

Since certain phenols, especially chlorophenols, are known to be toxic substances to larvae, the linking described in Part I has been developed with halogenophenols and tested for mothproofing.

Experimental

The materials used, method of application of formaldehyde and phenols to wool, the tests of fastness, the estimation of polymer formation, and the microscopic examination of the fibers are the same as in Part I [19].

Testing the Mothproof

All mothproofing tests were done by the Wool Industries Research Association, Leeds, England, according to the method described by Hartley, Elsworth, and Barritt [17], which is based on the earlier methods of Burgess [7] and Stiteler [33]. The sample of the fabric to be tested is placed in a Petri dish. Over the fabric is a brass tube (1½ in. diameter × 1 in. long) which is covered at the upper end by fine wire gauze. Ten vigorous half-grown *Tinola bisselliella* larvae are placed in the brass tube, which is then maintained at 21°C for 14 days. The degree of mothproofing is assessed by visual examination of the fabric, the amount of excrement, and the state of the larvae. An adequately mothproofed sample shows no visual signs of damage, there is only a trace of excrement, and most of the larvae will have died or pupated. With an unproofed sample there are many holes eaten in the fabric, much excrement is present, and some, but not necessarily all, of the larvae are still active.

Alkali Solubility [16]

The sample, of known dry weight, was treated for 1 hr. at 50°C with 0.10*N* sodium hydroxide at a liquor-to-wool ratio of 100:1. The wool was recovered in a Büchner funnel, washed free from alkali, and dried at 110°C. The alkali solubility is expressed as the percentage loss in weight.

Wet Abrasion-Resistance

The knitted fabric was abraded on a T.B.L.* ring wear tester against a standard woven wool fabric, and the number of revolutions to produce a hole recorded. The specimen was impregnated with a buffer solution at pH 7 and kept wet throughout the test. The results are means of ten determinations, and are expressed as percentages of the number of revolutions required to wear an untreated fabric.

Results

The Reaction of Wool Keratin with Phenols and Formaldehyde

Experiments using simple phenols, chlorophenols, and bromophenols show that the weight increases obtained are unstable to acid boiling but fairly fast to

* Tootal Broadhurst Lee.

TABLE I. PHENOLS LINKED TO WOOL BY FORMALDEHYDE AND THEIR FASTNESS

Treatment	Weight change (%) Initial	After soap wash	After acid boil
o-Chlorophenol	−0.17	—	—
o-Chlorophenol+HCHO	+0.74	+0.51	−0.21
2,4-Dichlorophenol	−0.06	—	—
2,4-Dichlorophenol+HCHO	+1.34	+1.31	0.0
2,4,6-Trichlorophenol	−0.71	—	—
2,4,6-Trichlorophenol+HCHO	+0.98	+0.85	−0.10
p-Chloro-*m*-cresol	+0.21	—	—
p-Chloro-*m*-cresol+HCHO	+1.97	+1.74	+0.16
4-Chlororesorcinol	−0.19	—	—
4-Chlororesorcinol+HCHO	+3.76	+3.76	+1.98
α-Chloro-β-naphthol	+0.61	−0.34	−0.21
α-Chloro-β-naphthol+HCHO	+5.42	+1.67	+0.85
p-Bromophenol	−0.47	—	—
p-Bromophenol+HCHO	+1.55	+0.66	+0.21
Resorcinol	+0.4	+0.1	−0.4
Resorcinol+HCHO	+3.0	+3.0	+0.2
α-Naphthol	+0.9	+0.2	+0.1
α-Naphthol+HCHO	+16.0	+16.0	+15.0

soap washing (Table I). The wool was treated in an aqueous or aqueous/alcoholic solution, 0.133*M* with respect to both formaldehyde and the chlorophenol, at 60°C for 30 min. and at a liquor-to-wool ratio of 50:1.

TABLE II. STABILITY TO DRY-CLEANING SOLVENTS

Treatment	Weight increase (%) Initial	After White Spirit	After trichlorethylene
2,4-Dichlorophenol+HCHO	1.31	1.02	1.10
2,4,6-Trichlorophenol+HCHO	1.01	0.96	0.80
4-Chlororesorcinol+HCHO	3.62	3.12	3.00
α-Chloro-β-naphthol+HCHO	5.61	5.41	4.87
p-Bromophenol+HCHO	1.33	1.26	1.06
Resorcinol+HCHO	3.0	3.0	3.0
α-Naphthol+HCHO	16.0	16.0	15.9

None of the solutions were buffered, and in all cases the pH remained between 5.8 and 6.8 throughout the reaction.

The fastness to solvents usually employed for dry-cleaning purposes is shown in Table II for several treatments.

Resistance of Treated Wools to Attack by Tineola bisselliella

The results of mothproofing tests on fabric treated by the methods previously shown to give good weight increases are given in Table III. The samples were all rinsed in alcohol before testing to re-

TABLE III. MOTHPROOFING OF TREATED WOOLS

Treatment	Weight increase (%)	Visual assessment: Damage	Excrement	Condition of larvae	Remarks
Resorcinol (*A*)	0.44	Considerable damage	Fairly large amount	6 active 4 pupated	Poor resistance
Resorcinol+HCHO (*B*)	3.61	5 small holes	Moderate amount	5 active 3 pupated 2 dead	Moderate resistance
α-Naphthol (*C*)+HCHO	15.27	Very slight damage	Small amount	2 active 8 pupated	Satisfactorily proofed
o-Chlorophenol (*D*)+HCHO	0.7	Considerable damage	Large amount	6 active 4 pupated	Poor resistance
2,4-Dichlorophenol (*E*)+HCHO	1.18	1 hole	Small amount	3 active 5 pupated 2 dead	Satisfactorily proofed
2,4,6-Trichlorophenol (*F*)+HCHO	1.10	No visible damage	Small amount	3 active 3 pupated 4 dead	Satisfactorily proofed
4-Chlororesorcinol (*G*)+HCHO	3.52	No visible damage	Small amount	1 active 7 pupated 2 dead	Satisfactorily proofed
α-Chloro-β-naphthol (*H*)+HCHO	5.11	2 holes	Small amount	2 active 7 pupated	Moderate resistance
p-Bromophenol (*J*)+HCHO	1.48	2 small holes	Small amount	3 active 5 pupated 2 dead	Fairly satisfactorily proofed
HCHO (*K*)	0.50	Considerable damage	Very large amount	6 active 4 pupated	Very poor resistance
Untreated (*L*)	zero	Very great damage	Very large amount	3 active 6 pupated	Very poor resistance

move any loosely held phenol. The corresponding weight increase of the same treated sample is also given. Samples treated with a phenol alone, without formaldehyde, all showed no mothproofing, and only one such result is given, that of resorcinol. The samples after completion of the mothproofing tests are illustrated in Figure 1.

The effect of subsequent treatment on fabric initially treated with formaldehyde and 2,4,6-trichlorophenol is given in Table IV, the samples being illustrated in Figure 2.

The sulfuric acid dyeing is with 1% Azogeranine B, the acetic acid dyeing with 1% Coomassie Fast Yellow R, and the neutral dyeing with 0.3% Fast Acid Violet A2B, 0.5% Coomassie Blue BL, and 4% Milling Red R.

The stability of the mothproofing resistance to dry-cleaning solvents is shown in Table V, the samples being illustrated in Figure 3. A control sample was included because the damage was somewhat greater than usual. The initial treatment was 2,4,6-trichlorophenol + formaldehyde.

Estimation of Polymer Formation

The titration figures and over-all loss of formaldehyde from several phenol-formaldehyde baths are recorded in Table VI. The liquors are all strong, being 0.33*M* with respect to both the phenol and formaldehyde. The treatment was at 60°C and neutrality (no buffer).

Microscopic Examination of Fibers

The fibers of several treatments were examined for any signs of scale stripping or masking—two

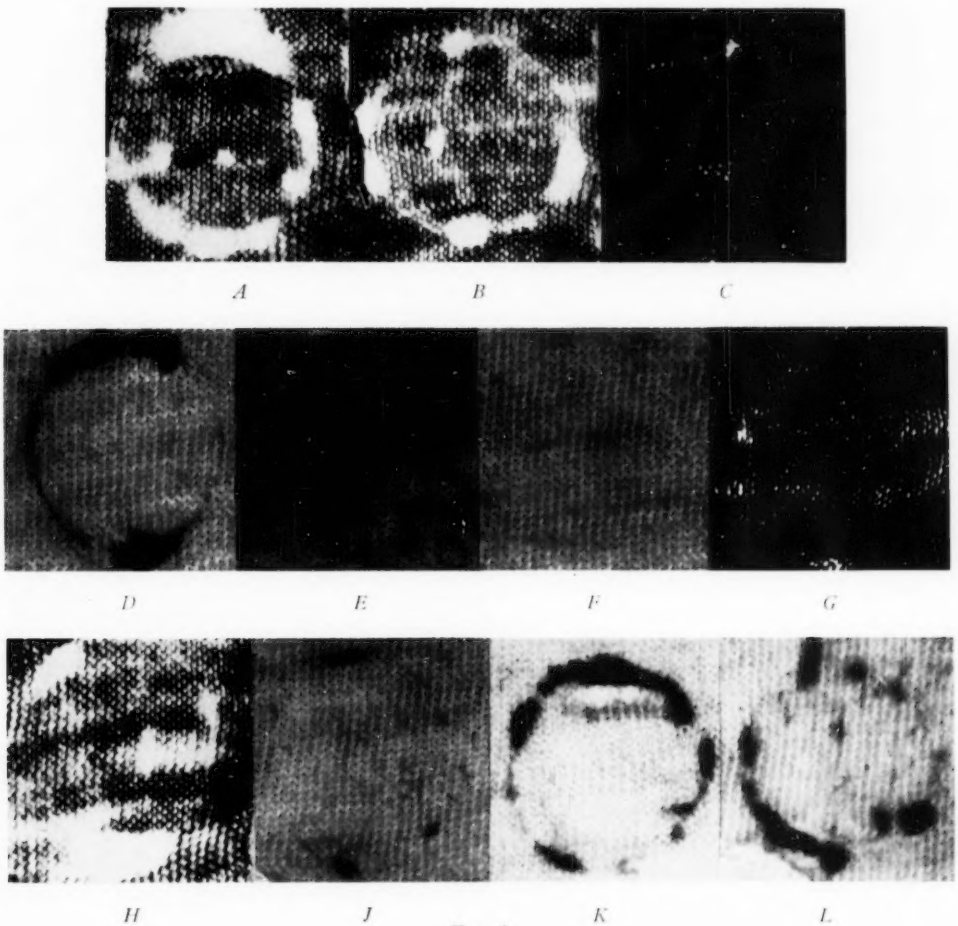
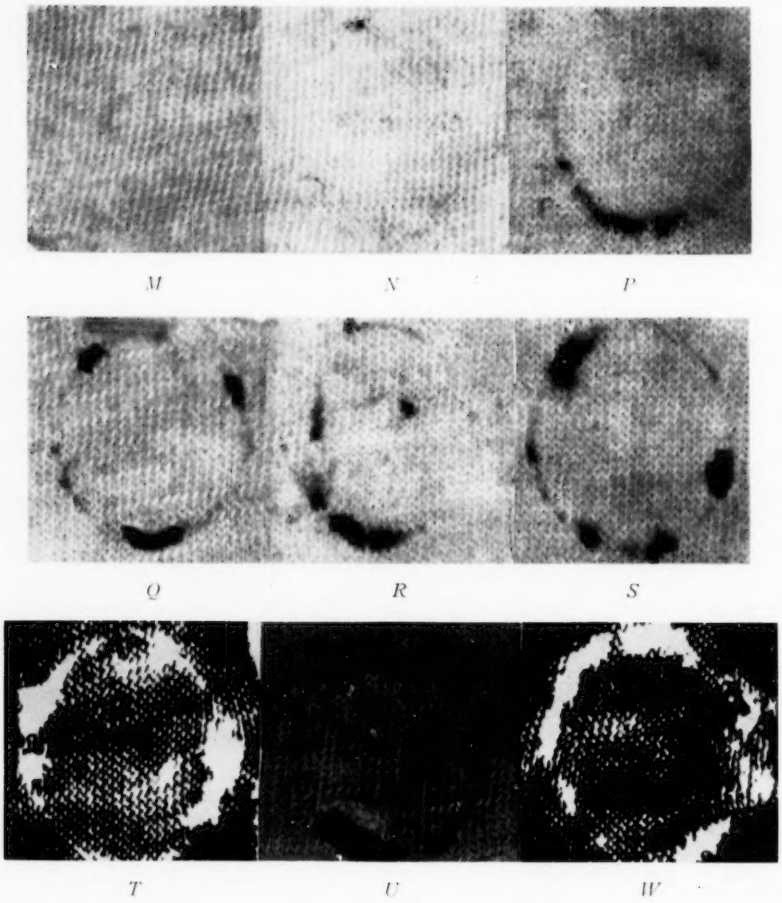


FIG. 1



M *N* *P*

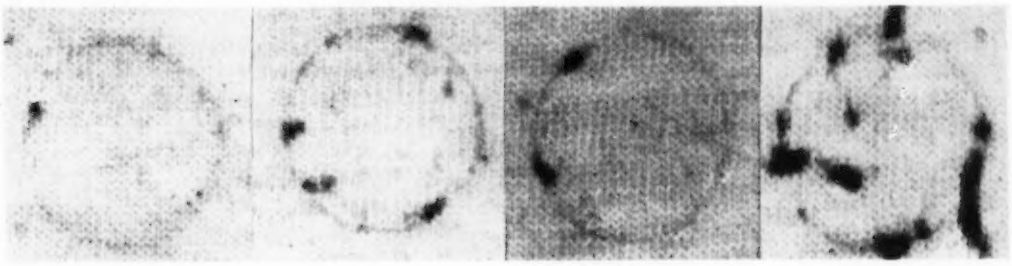
Q *R* *S*

T *U* *W*

FIG. 2

TABLE IV. EFFECT OF SUBSEQUENT TREATMENT ON MOTHPROOFING

Second treatment	Visual assessment		Condition of larvae	Remarks
	Damage	Excrement		
1 wash (*M*)	Slight damage	Very small amount	6 pupated 4 dead	Satisfactorily proofed
2 washes (*N*)	1 pinhole	Small amount	1 active 4 pupated 5 dead	Satisfactorily proofed
3 washes (*P*)	3 small holes	Small amount	10 pupated	Fairly satisfactorily proofed
4 washes (*Q*)	3 holes	Moderate amount	10 pupated	Moderate resistance
5 washes (*R*)	4 holes	Moderate amount	2 active 8 pupated	Moderate resistance
6 washes (*S*)	Numerous holes	Large amount	2 active 8 pupated	Poor resistance
Dyeing in H_2SO_4 (*T*)	4 large holes	Large amount	1 active 8 pupated 1 dead	Poor resistance
Dyeing in CH_3COOH (*U*)	Numerous holes	Large amount	2 active 7 pupated 1 dead	Poor resistance
Neutral dyeing (*W*)	3 small holes	Moderate amount	3 active 4 pupated 3 dead	Fairly satisfactorily proofed



X *Y* *Z* *Control*

FIG. 3

TABLE V. EFFECT OF DRY-CLEANING SOLVENTS ON MOTHPROOFING

Solvent	Visual assessment: Damage	Visual assessment: Excrement	Condition of larvae	Remarks
None (*X*)	1 small hole	Small amount	3 active 4 pupated 1 dead	Satisfactorily proofed
White Spirit (*Y*)	6 holes	Moderate amount	4 active 5 pupated 1 dead	Moderate resistance
Trichlorethylene (*Z*)	2 small holes	Fairly small amount	4 active 4 pupated 2 dead	Moderate resistance
Control sample	Numerous large holes	Large amount	2 active 8 pupated	Poor resistance

TABLE VI. LOSS OF FREE FORMALDEHYDE BY POLYMERIZATION

Phenol	Titer: Initial	Titer: 30 min.	Titer: 60 min.	Loss of HCHO (%)
Resorcinol	11.7	11.8	11.1	5.1
α-Naphthol	11.5	10.4	8.2	28.7
2,4-Dichlorophenol	11.8	10.55	10.45	11.4
2,4,6-Trichlorophenol	11.5	11.5	11.5	nil
p-Bromophenol	11.7	11.85	11.85	nil

TABLE VII. MICROSCOPIC EXAMINATION OF FIBERS

Treatment	Unmodified (%)	Modified (%)
None	89	11
Resorcinol+HCHO	87	13
α-Naphthol+HCHO	4	96
2,4-Dichlorophenol+HCHO	84	16
2,4,6-Trichlorophenol+HCHO	88	12
p-Bromophenol+HCHO	89	11

typical results of the deposition of polymers. The results of these microscopic counts are given in Table VII.

TABLE VIII. PROPERTIES OF TREATED FABRICS

Treatment	Alkali solubility (%)	Abrasion-resistance (%)
None	10.0	100
HCHO	3.06	326
Resorcinol+HCHO	4.24	207
2,4-Dichlorophenol+HCHO	7.01	190
2,4,6-Trichlorophenol+HCHO	7.75	185
p-Bromophenol+HCHO	4.00	224
4-Chlororesorcinol+HCHO	7.34	200

Properties of Treated Fabrics

The alkali solubilities and wet abrasion-resistances of several treated fabrics are given in Table VIII.

Discussion

The treatment of wool with formaldehyde and phenols gives rise to weight increases which are stable to subsequent hot alkaline hydrolysis or solvent extraction but are broken by hot acids, with liberation of the phenol [19]. It has been shown that this reaction also holds for several halogenophenols, and that in all cases reaction of the wool

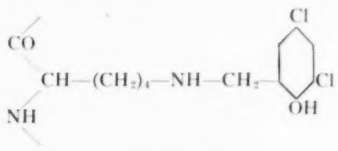
with formaldehyde and a phenol gives a greater weight increase than the corresponding reaction with the phenol alone. The stability of these weight increases is the same as that of simple phenols, and corresponds to that expected for a covalent methylene bridge between the phenol and the ε-amino groups of the lysine residues in the wool keratin [12].

When wool is treated with formaldehyde and halogenophenols under mild conditions, it is shown that a good resistance to the common clothes moth, *Tinecola bisselliella*, is obtained. This resistance is only slightly impaired by successive alkaline washes, subsequent neutral or alkaline treatments, or solvents used for dry-cleaning, but is completely removed by hot acids or any subsequent hot acidic treatment such as acid dyeing. Similar treatments using phenols alone or formaldehyde alone give no resistance to attack by the larvae. The weight increase of 0.5% obtained on treatment with formaldehyde alone is consistent with the cross-linking found by Alexander, Carter, and Johnson [1], and is in no way responsible for any part of the mothproofing obtained by McLean and Traill [26]. Since the stability of the mothproofing is the same as that of the weight increases due to linking of the phenols, it can be assumed that the resistance obtained is due to the covalent linking of the toxic substances (phenols and halogenophenols), as was suggested in the Introduction. The linkage is expected to be broken by hot acidic treatments, and this is confirmed by the mothproofing tests.

Analysis of the formaldehyde content of the liquors used for treatments shows that there is no condensation and polymerization, except in the case of α-naphthol, and this has already been shown [19]. Microscopic examination of the fibers of treated fabrics also confirms this view.

The properties of the treated wools all show a reduction in alkali solubility, although this is not as low as that obtained with formaldehyde alone, and an increase in wet abrasion-resistance, but less than that obtained with formaldehyde alone. This would seem to indicate that some of the lysine groups which react with formaldehyde alone to give lysine-methylene-tyrosine cross-links [1] react with the phenol to give lysine-methylene-phenol links. The remainder give the internal cross-link and cause the reduced alkali solubility and increased wet abrasion-resistance. This additional reaction when formaldehyde is used in reactions involving wool keratin has previously been shown by Earland and Johnson in an antishrink reaction using formaldehyde and sodium chlorite [9].

Consideration of all the findings makes it highly probable that the reactions found by Fraenkel-Conrat and Olcott [12] for other proteins and Johnson [19] for wool keratin also apply to the reactions with halogenophenols and formaldehyde and that covalent-linked mothproofing agents are formed—*e.g.*,



Summary

It has been shown that reactions of phenols or halogenophenols and formaldehyde with wool keratin give greater weight increases than the corresponding reactions with the phenols alone, and that this is not due to the deposition of polymers.

This weight increase is stable to subsequent alkaline hydrolysis or extraction with organic solvents, but is readily removed by warm acid hydrolysis.

Synonymous with this weight increase is a resistance to the attack of clothes moth larvae, *Tinecola bisselliella*. The stability of the mothproofing is identical with that of the weight increase.

It seems probable that covalent links are formed between the toxic compounds (phenols and halogenophenols) and the ε-amino groups of the lysine residues in the wool keratin.

Acknowledgments

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(Manuscript received March 24, 1953.)

Part III: The Coupling of Linked Phenols to Give Covalent Linked Dyes

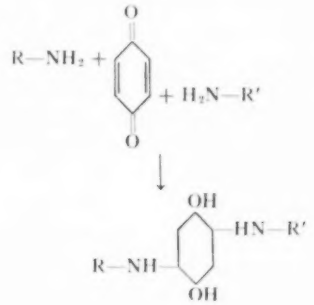
Abstract

It is shown that phenols which are covalently linked into wool keratin may be coupled with diazonium compounds to give covalently linked dyes. In addition to the many simple phenols which have been shown in Parts I and II [10, 11] to link covalently, the amides of hydroxynaphthoic acid are linked in this manner and are shown to give good colorations which are fast to subsequent alkaline washing.

Introduction

There have been several attempts to produce chemically linked colors in wool keratin in order to obtain dyed fibers which are permanent to all subsequent treatments.

As early as 1913, Scharvin [17] noticed that wool can be dyed in a hot aqueous solution of *p*-benzoquinone. The color produced was deep brown and fast to alkaline and acid washing as well as boiling alcohol. He showed that other quinones could also be used, and considered the reaction to be proof of the presence of active amino groups in the fiber, a substituted aminoquinone being formed. Barr and Speakman [2] described this reaction as being a cross-linkage formation between two amino groups:

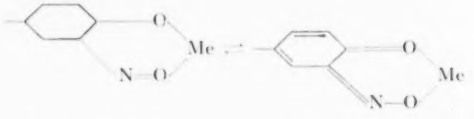


Stoves [19] has also shown that this reaction is probable, but that most of the benzoquinone is present in the wool as a polymer within the fiber and not as a cross-link.

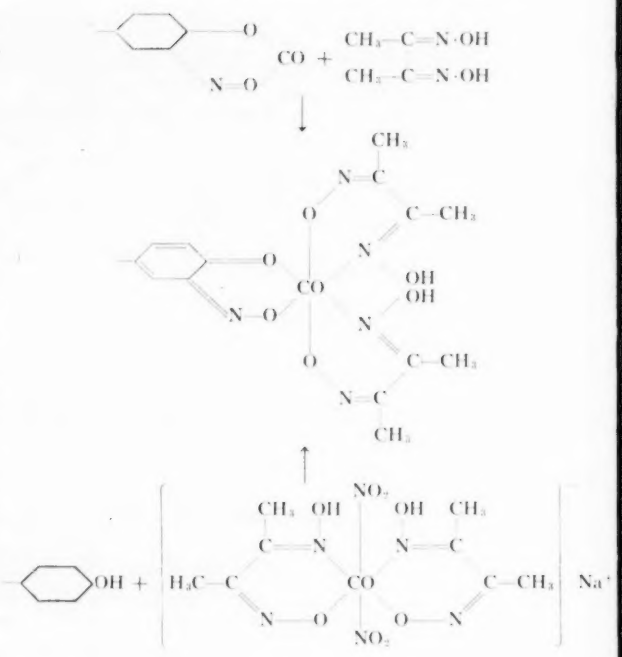
Fort and Lloyd [6] in 1914 dyed wool with indigo, extracted with glacial acetic acid, and obtained on dilution a substance which appeared to be an indigo-wool substance. They obtained consistent results, with an average of 38.1% wool substance. Similar results were obtained by extracting with boiling pyridine, and they suggested chemical combination of indigo with keratin, followed by hydrolysis within the keratin molecule.

In 1932 Temmink Groll [20] treated wool with dilute sodium hydroxide, a phenol, and sodium hypochlorite. He found that α-naphthol gave a coloration that was red, β-naphthol and thymol yellow-orange, phenol green, and resorcinol brown. The basis of this coloration is the Sakaguchi reaction [15] with the guanidyl group of arginine. Sakaguchi obtained a substance of approximate formula $C_{22}H_{18}N_2C10_4$ on treating arginine with α-naphthol, sodium hydroxide, and sodium hypochlorite.

Probably the most outstanding contribution to the production of chemically linked colors in wool keratin is the work of Nilssen [14]. He treated wool at 50°–70°C for 5–10 min. with nitrous acid and a metallic salt, and obtained a coloration due to tautomerism of the *o*-nitroso tyrosine derivative with the *o*-quinone-monoxime of tyrosine:



where Me is a metal. Similar colors were obtained with tyrosine itself and also with silk fibroin, but no coloration is obtained with gelatin. The coloration may be further developed by treatment with mordant dyes or dimethylglyoxime with the cobalt derivative. With the latter, the same brown shade is obtained by following the preliminary treatment wth a dimethylglyoxime treatment or by direct treatment with sodium-*bis*-dimethylglyoxime-dinitro-cobaltiate and acetic acid. The amount of metal taken up is sufficient in all cases to account for only 50%–60% of the tyrosine present. The washfastness of all these colors is excellent, and the lightfastness ranges from good to very good.



The use of azo compounds for producing colors in wool has been demonstrated by Small and Philpot [18] and Glynn [8]. Small and Philpot showed that after prolonged treatment with nitrous acid the tyrosine is converted to the *o*-diazophenol, which will then couple with β-naphthol, resorcinol, or α-naphthylamine. Glynn [8] used diazonium compounds for the determination of wool damage by showing that chemical coupling resulting in permanent coloration is greater in damaged wools. The coupling takes place in the *o*-position to the tyrosine hydroxyl group.

The amino and tyrosine groups of wool keratin have been dinitrophenylated by Sanger [16] and Farnworth and Speakman [5] by treatment with 2,4-dinitrofluorobenzene. This results in a yellowish-brown coloration which is fast. Blackburn [3] has shown that proteins thus treated can be hydrolyzed by acid without breaking the protein-dinitrobenzene links, the hydrolysis product still retaining the coloration.

In some cases there is undoubtedly a complex combination of keratin, metal, and dye obtained when the metallized azo dyes are applied to wool, although the exact reaction is unknown.

The Dyeing of Azoic Colors

Dyeing with azoic colors consists of impregnating the material with a phenol and subsequently treating with diazonium compounds to form insoluble azo dyes on the fibers. Since this necessitates treatment in fairly strong alkaline solution, the use of azoic colors has been limited almost entirely to cotton. In dyeing cotton by this method, formaldehyde is often added to the initial impregnating liquor because it is claimed to condense two phenol molecules together, thus giving a less soluble product.

Protection against damage in wool was mentioned by Lint [13]. Leitch and Company [12] described the use of suspensions of naphthols in soap solution in preference to solutions in strong alkali. Turner [22] described a method of dyeing wool with azoic colors, incorporating the use of relatively strong solutions of sodium chloride to prevent swelling and damage to the fibers. He also used formaldehyde with the initial naphthol treatment, but gave no explanation for its use; it is presumably by analogy with the method employed for cotton. He claimed the colors obtained on wool were faster than those on cotton.

By a modification of the lysine-tyrosine linking in proteins [7], and in particular in wool [1], the present author has previously shown [10, 11] that phenols may be covalently linked into wool keratin by using formaldehyde. The possibility of coupling the linked wool in alkaline solution with diazotized amines forms the basis of the present study, which is the same as Turner's [22], although Turner did not consider the mechanism, but only the result.

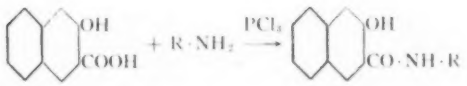
Experimental

Materials

The fabric was the same as that used in Part I [10]. The phenols and amines used were of Analar or B.P. quality and the sodium nitrite was of Analar quality.

Preparation of Amides

The *N*-arylamides of 2-hydroxy-3-naphthoic acid were prepared by adding 1 mol of phosphorus trichloride drop by drop to a stirred suspension of 2 mols 2-hydroxy-3-naphthoic acid and 2 mols amine in xylene at 60°–70°C. After addition the mixture was heated to 110°–120°C with stirring, cooled, and the amide filtered off and recrystallized from chlorobenzene [4, 23].



Initial Wool Treatments

The wool was stirred in an aqueous or aqueous/alcoholic solution 0.133*M* with respect to the phenol and formaldehyde (if used) at 60°C for 30 min., the liquor-to-wool ratio being 30:1. It was then rinsed in alcohol, and thoroughly washed in running water for 1 day to remove any loosely bound phenol. Weight increases were determined by drying to constant weight at 110°C both before and after treating.

Coupling Reactions

The treated wool was immersed in *N* NaOH at 0°–5°C at a liquor-to-wool ratio of 20:1. A solution of the diazotized amine containing 0.1 g. of amine in 20 ml. of *N* HCl per gram of wool was then added with stirring, and the whole was stirred for 5 min. In some cases addition of a small amount of NaOH or HCl was necessary to effect coupling. After coupling, the wool was washed in running water for a few minutes, washed in 0.5% soap solution at 40°C for 10 min. to remove excess amine, diazo compound, or loose color, and dried at 110°C.

The nitranilines were diazotized by dissolving in a small amount of hot concentrated HCl, diluting to about 3*N*, cooling to 10°C, and treating with cold strong $NaNO_2$ solution. Sulfanilic acid and naphthionic acid were dissolved in 2*N* NaOH, the nitrite solution was added, the whole cooled to 6°C, excess 2*N* HCl previously cooled to 0°C added, and the whole allowed to rise to 10°C. All the other amines were diazotized in *N* HCl with strong $NaNO_2$ solution at the temperatures given in Table I [21].

TABLE I. TEMPERATURES OF DIAZOTIZATION

Amine	Temperature (°C)
Toluidines	−5 to −2
Aniline; chloranilines	0
Naphthylamines; dianisidines	10
Benzidine	12 to 15

TABLE II. TREATMENT WITH FORMALDEHYDE AND 2-HYDROXY-3-NAPHTHOIC ACID DERIVATIVES

Treatment	Weight increase (%)
2-Hydroxy-3-naphthoic acid	0.95
2-Hydroxy-3-naphthoic acid+HCHO	8.37
H.N.A.* anilide	1.11
H.N.A. anilide+HCHO	6.07
H.N.A. 5-chloro-*o*-toluidide	1.01
H.N.A. 5-chloro-*o*-toluidide+HCHO	4.77
H.N.A. α-naphthylamide	2.64
H.N.A. α-naphthylamide+HCHO	2.90
H.N.A. *o*-toluidide	1.84
H.N.A. *o*-toluidide+HCHO	6.21

* H.N.A. = 2-Hydroxy-3-naphthoic acid.

Washfastness Test

The treated and coupled wool was stirred gently for 30 min. in a 1% soap solution at 70°C, at a liquor-to-wool ratio of 50:1

Alkali Solubility

The alkali solubility was determined according to the method of Harris and Smith [9].

Wet Abrasion-Resistance

The wet abrasion-resistance was determined as in Part II [11].

Results

The reaction of wool keratin with phenols and formaldehyde has been studied [10], and the weight increases obtained with many simple phenols are known. In addition to several of these, 2-hydroxy-3-naphthoic acid and its arylamides were found to give good colorations on coupling with treated wool. The weight increases obtained with these compounds are given in Table II.

Wool samples treated with several of the simple phenols and 2-hydroxy-3-naphthoic acid and its arylamides, both with and without formaldehyde, were coupled with a range of amines. A wide range of both phenols and amines were chosen so that few are repeated. Comparison is made throughout with treatments employing formaldehyde and treatments without formaldehyde. Table III gives the colorations produced and shows in all cases that initial treatment with formaldehyde and the phenol gives a deeper color than that obtained with the phenol alone.

Properties of the Treated Wools

The alkali solubility and wet abrasion-resistance of several of the treated and coupled wools were determined, and the results are given in Table IV.

TABLE III. COLORATIONS PRODUCED ON COUPLING PHENOL-TREATED WOOLS

Initial treatment	Coupling amine	Coloration	
		Before washing	After washing
o-Cresol	benzidine	nil	nil
o-Cresol+HCHO	benzidine	nil	nil
m-Cresol	β-naphthylamine	pale pink	nil
m-Cresol+HCHO	β-naphthylamine	brown	brown
p-Cresol	aniline	nil	nil
p-Cresol+HCHO	aniline	nil	nil
Resorcinol	aniline	pale orange	yellow
Resorcinol+HCHO	aniline	deep brown	deep brown
Phloroglucinol	*o*-dianisidine	pale brown	pale brown
Phloroglucinol+HCHO	*o*-dianisidine	brown	brown
α-Naphthol	*m*-chloraniline	pink	pink
α-Naphthol+HCHO	*m*-chloraniline	deep red	deep red
β-Naphthol	α-naphthylamine	pink	pale pink
β-Naphthol+HCHO	α-naphthylamine	brick red	brick red
2-Hydroxy-3-naphthoic acid	*m*-chloraniline	red	pink
2-Hydroxy-3-naphthoic acid+HCHO	*m*-chloraniline	deep red	deep red
H.N.A. anilide	*p*-nitraniline	orange	pale orange
H.N.A. anilide+HCHO	*p*-nitraniline	red	red
H.N.A. *o*-toluidide	*m*-toluidine	orange	orange
H.N.A. *o*-toluidide+HCHO	*m*-toluidine	deep red	deep red
H.N.A. 5-chloro-*o*-toluidide	*o*-chloraniline	orange	pale orange
H.N.A. 5-chloro-*o*-toluidide+HCHO	*o*-chloraniline	brilliant red	brilliant red
H.N.A. α-naphthylamide	naphthionic acid	pale yellow	nil
H.N.A. α-naphthylamide+HCHO	naphthionic acid	puce	puce

TABLE IV. PROPERTIES OF TREATED WOOLS

Initial treatment	Coupling amine	Alkali solubility (%)	Abrasion-resistance (%)
None	None	10.0	100
HCHO	None	3.06	326
Resorcinol+HCHO	aniline	4.64	265
Phloroglucinol+HCHO	*o*-dianisidine	4.84	208
H.N.A.+HCHO	*m*-chloraniline	5.92	200
H.N.A. 5-chloro-*o*-toluidide+HCHO	*o*-chloraniline	6.66	196
H.N.A. α-naphthylamide+HCHO	naphthionic acid	6.62	188

Discussion

The results found for many simple phenols [10] and halogenophenols [11] are found to hold for larger substituted phenols, such as 2-hydroxy-3-naphthoic acid and its arylamides. These are also linked to wool keratin by formaldehyde, the weight increases being greater when formaldehyde is added to the liquor used for treatment.

It is shown that the suggested use of linked phenols in producing covalent-linked dyes is possible. The formation of washfast coloration on treating wool which has been reacted with formaldehyde and a phenol with a diazotized amine is demonstrated. Several phenols were used for the initial treatments and several amines for the final coupling reactions, and it was found that the best colors are obtained when the arylamides of 2-hydroxy-3-naphthoic acid are used. The colorations produced have a good fastness to soap washing, and initial reaction with formaldehyde and the phenol is superior to reaction with the phenol alone. The colorations produced are in good agreement with those expected from the postulated link, and a method of introducing covalent-linked dyes into wool keratin is suggested. Unfortunately, it is impossible to investigate the stability of the coloration to hot acid solutions, since any liberation of an azo compound into the liquor would set up ordinary acid dye bath conditions and the color would thus return to the wool. The method does, however, give a means of obtaining colors that are fast to hot alkaline solutions, which are the most disastrous to wools dyed in the normal way with azo compounds.

It is interesting to note that these results confirm those of Turner [22], who found that very fast colors were obtained using the azoic method with formaldehyde in the initial bath.

Consideration of the results obtained point to the probability that the method of introducing phenols into proteins described by Fraenkel-Conrat and Olcott [7] and previously shown in wool by the present author [10] can be applied to the formation of covalent-linked dyes in the keratin molecule. This link would be a methylene bridge between the ε-amino group of the lysine residues in wool keratin and the phenol nucleus. No actual formula can be postulated, however, because it would be extremely difficult to determine the exact position of both the linking bridge and the coupling azo group.

Summary

Colorations that are fast to alkaline washing can be produced by coupling in alkaline solution wool that has previously been treated with formaldehyde and a phenol with a diazotized amine in acid solution.

With all the phenols and amines examined, better results are produced if the initial treatment is carried out in the presence of formaldehyde, the best results being obtained with 2-hydroxy-3-naphthoic acid and its arylamides.

It is suggested that covalent-linked dyes are formed with the wool keratin molecule.

Acknowledgment

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The Reaction of Polyacrylic Acid with Nylon

A. C. Nuessle and R. F. Crawford*

Textile Applications Laboratory, Rohm & Haas Company, Philadelphia, Pennsylvania

POLYACRYLIC ACID is a relatively new chemical of commerce. Only a few years ago it was scarcely more than a laboratory curiosity, but now it is used widely as a warp size and single-end size for hydrophobic fibers [2]. Originally designed for use on nylon, it has more recently shown some promise on Orlon, Acrilan, and other synthetics. The present discussion, however, relates not to its proven utility as a size, but to its possible use as a finish, based on what appears to be a chemical combination between polyacrylic acid and nylon.

The Effect

When a nylon fabric is padded through a dilute solution of polyacrylic acid and dried, it becomes quite stiff, due to the bonding of the fibers and yarns into a rigid structure. Any polymeric sizing agent would tend to give such stiffening, but polyacrylic acid is unusually effective, presumably because of its great specific adhesion to nylon [4]. Even more important to the present discussion is the fact that, whereas *PAA* dried onto nylon under normal drying conditions (*e.g.*, 240°F) can readily be scoured off, *PAA* heat-set onto nylon (*e.g.*, at 400°F) is extremely difficult to remove. This effect is rather unique; for example, it is not shown to any great extent by polymethacrylic acid. Typical data on the effect of 5% *PAA** applied to nylon taffeta under various curing conditions are presented in Table I and plotted in Figure 1. The wash was a normal Laundromat cycle (7 min. tumbling in 0.1% soap

* Present address: American Viscose Corp., Marcus Hook, Pa.

* The polyacrylic acid used in these experiments was Acrysol A-1 (Rohm & Haas).

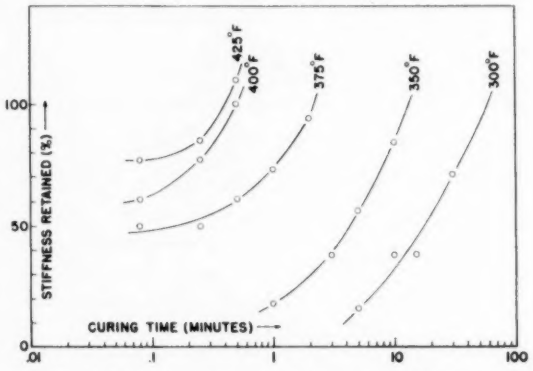

FIG. 1. *Effect of curing conditions on stiffness retention of nylon fabric padded with polyacrylic acid.*

solution and 0.1% soda ash at 140°F, followed by 19 min. rinsing).

It will be observed that the stiffness retained increases with the severity of the cure, good retention being obtained only under extreme conditions of time or temperature. The curing time necessary to attain 100% stiffness retention at each curing temperature can be estimated roughly from the curves of Figure 1. The values are listed in Table II.

These conditions, while apparently quite severe, are not much more severe than those of normal nylon heat-setting. Moreover, 100% stiffness retention in the case of a 140°F tumble wash is a very unusual accomplishment. Therefore, the possible utility of such a treatment as a durable nylon finish appeared worthy of further investigation. In the course of this work, insight into the possible mechanism of the insolubilization was obtained. It is hoped that these findings may have technological or scientific interest.

TABLE I. EFFECT OF CURING CONDITIONS ON THE DURABILITY OF POLYACRYLIC ACID ON NYLON FABRIC

Curing time (min.)	Curing temp. (°F)	Stiffness Gurley (mg./in.) Unwashed	Stiffness Gurley (mg./in.) Washed	Stiffness retained* (%)
10	240	16	1†	6†
5	300	19	3	16
10	300	13	5	38
15	300	16	6	38
30	300	17	12	71
1	350	17	3	18
3	350	16	6	38
5	350	18	10	56
10	350	19	16	84
0.08	375	16	8	50
0.25	375	16	8	50
0.5	375	18	11	61
1	375	15	11	73
2	375	17	16	94
0.08	400	18	11	61
0.25	400	17	13	77
0.5	400	17	17	100
0.08	425	17	13	77
0.25	425	20	17	85
0.5	425	19	21	110
Untreated fabric				
10	240	2	1	—
0.08	425	2	1	—

* (Washed stiffness/original stiffness) × 100.

† The residual stiffness was due to the fabric itself; the size had been completely removed.

Theoretical Aspects

Reduction in Carboxyl Content

The insolubilization of polyacrylic acid must involve either cross-linking of the *PAA* itself—*e.g.*, through anhydride formation—or reaction of the *PAA* with the nylon. In either case, there would be a reduction in the free carboxyl content. The data presented in Table III show that such is the case, although it is apparent that only a small proportion of the total acidity is thus involved.

In this experiment, nylon fabric was padded through a 10% solution of *PAA* (40% wet pickup) and divided into three sections for curing. The subsequent analysis was conducted as follows: sections of each fabric were placed in covered flasks containing a measured amount of dilute (0.05*N*) sodium hydroxide, in a slight stoichiometric excess over the expected *PAA* content. As a control, the same amount of caustic was put into a similar flask alongside the others. The contents of each flask were boiled for 15 min., and allowed to stand an additional 30 min. A small amount of sodium chloride was added to give a sharper end-point (by repressing the ionization of sodium polyacrylate), and the solutions were then titrated with standard sulfuric acid, using phenolphthalein indicator. The free carboxyl content of the fabric (expressed as acrylic

TABLE II. CURING TIME *vs.* TEMPERATURE TO EFFECT 100% STIFFNESS RETENTION AFTER ONE LAUNDROMAT WASH

Temperature (°F)	Time (min.)	Time (sec.)
300	60	
350	13	
375	2.2	132
400	0.5	30
425	0.4	24

TABLE III. REDUCTION IN CARBOXYL CONTENT ON CURING

Curing time (min.)	Temp. (°F)	Acidity (as CH_2=CH·COOH) (%)
10	240	3.90
60	300	3.80
0.5	400	3.55

acid) may be calculated from the difference between the amount of acid required for the control and that required for a given fabric:

$$\% \ AA = \frac{(B - A) \times N \times 0.072 \times 100}{W},$$

where A = cc. H_2SO_4 required for the sample, B = cc. H_2SO_4 required for the control, N = normality of the acid, and W = weight of the fabric.

It is obvious that this free acidity represents carboxyl groups which had not reacted or which had reacted but which had been hydrolyzed during the analysis. Thus, the loss in carboxyls—*i.e.*, the difference between cured and uncured acidity—is an indication of the number of carboxyls which combined (either with the nylon or with each other) firmly enough to resist the alkali. From the data it would appear that only a small proportion of the carboxyls were so combined. Similar small differences in free acidity were obtained when the fabrics were immersed in an excess of 0.05*N* NaOH for 6 hrs. at room temperature. It should be pointed out that, in either case, not only were the cured fabrics still quite stiff after the analysis, but they were able to absorb copper ions from a solution of copper sulfate, indicating that the *PAA* had only been neutralized, not removed, by the alkali. More will be said about alkali resistance of the finish in a later section.

Effect on Other Fibers

If the mechanism involved only insolubilization of the polyacrylic acid, we might expect that the finish would be durable on other fibers. However, no appreciable durability could be demonstrated on fabrics made of acetate, Orlon, or Dacron. Apparently the basicity of the nylon is in some way involved in the adhesion of the finish, by either physical or chemical bonds. Applications to silk and wool have tended to substantiate this viewpoint. On silk, an interesting crispness may be obtained, the washfastness of which is limited only by the amount of curing the silk can stand.

On wool, the treatment imparts felt-resistance, accompanied, of course, by a very undesirable stiffness. On tumble washing, the fabric will gradually soften, while reasonable felt-resistance will be maintained through a number of additional washes. In one trial, untreated wool shrank 41% in area after 2 hrs. of tumble-washing in a nonionic detergent, and a total of 58% after an additional 2 hrs. in soap. Wool treated with 5% *PAA* (cured 60 min. at 300°F) shrank 0% and 6% when similarly washed. Despite the severe cure, the wool showed no obvious damage.

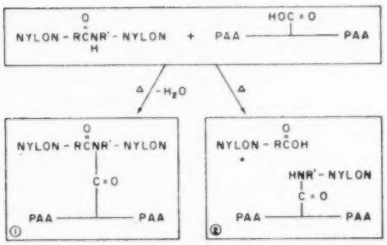

FIG. 2

Isolation of the Reaction Mixture

Additional evidence that the insolubilization of the finish on nylon is not due merely to anhydride formation can be obtained by extracting the treated fabric with boiling benzyl alcohol, a nylon solvent. This will dissolve the interior of the nylon fibers, leaving a gossamer-like residue which appears to be a *PAA*-nylon reaction product. In one instance where 5% *PAA* (on the weight of the nylon) had been applied, the residue amounted to 9.8%. It contained both nitrogen and unreacted carboxyls.

While the mechanism of the reaction has not been determined, two possibilities are (*1*) imide formation and (*2*) trans-amidization, as shown in Figure 2. The latter is the more plausible. A third possibility—that the combination takes place on end-groups—would give a result similar to (*2*) above.

Coreactions

Although the durability of the finish seems to be due to chemical reaction between the *PAA* and the surface molecules of the nylon, most of the carboxyls are not utilized, as shown by the analytical data above.

If we attempt to neutralize some of the excess acidity prior to application to the nylon, using ammonium or sodium hydroxide or an organic amine, the durability of the finish suffers. In fact, beyond about 25% neutralization, it is difficult to obtain any fixation whatsoever.

It has been found possible, however, to incorporate materials which will coreact with the polyacrylic

TABLE IV. REACTION OF *PAA* WITH ALCOHOLS AND AMIDES

Additive	Condition of films after 16 hrs. in water: Dried (infrared)	Dried and cured (10 min. at 350°F)
A. None	Dissolved	Very swollen and sticky
B. Methanol	Dissolved	Very swollen and sticky
C. Benzyl alcohol	Dissolved	Less swollen than A
D. Ethylene glycol	Swollen	Slightly swollen, slightly tacky
E. Glycerol	Swollen	Rather brittle particles
F. Sorbitol	Swollen	Like E, but yellowed
G. Hydroxyethylcellulose	Swollen	Rather soft particles
H. Formamide	Dissolved	White, tough, rubbery
I. Dicyandiamide	Dissolved	Extremely swollen, rubbery
J. Methacrylamide	White, opaque	Very slightly swollen
K. Urea	Dissolved	Soft, rubbery
L. Gelatin	Swollen	Rubbery, yellow

acid during the cure. Two classes of chemicals which may be utilized in this way are amides and alcohols. The varied efficiency of several members of these classes in insolubilizing polyacrylic acid may best be shown by drying down films of *PAA* containing the additive, *in the absence of nylon*. The films were prepared by pouring a 10:3 (solids ratio) mixture of *PAA*:additive onto glass plates and drying under infrared lamps. A duplicate set was subsequently cured 10 min. at 350°F in an oven. All films were then submerged in water and observed after 16 hrs. Table IV describes the physical appearance of the films.

The partial insolubilization of *PAA* by heat alone, without additive, is undoubtedly due to anhydride formation. Of the alcohols tested, glycerol and the other polyhydric materials appear to impart complete insolubilization plus a rather effective resistance to swelling. Ethylene glycol, although capable of cross-linking, is less efficient. The slight but noticeable effect of benzyl alcohol, which cannot cross-link, is probably due to the hydrophobicity of the ester.

Among the amides, the situation is somewhat more obscure. All tend to insolubilize when cured, but the degree of swelling is quite variable: formamide is more effective than would be expected, while dicyandiamide is much less so. Best results were obtained with methacrylamide and gelatin. The fact that all the amides show apparent reaction with *PAA* further substantiates the belief that nylon, a polyamide, undergoes a similar reaction.

When the above materials were cured onto nylon in conjunction with polyacrylic acid at a 10:3 solids ratio, only methanol lowered the crispness and durability of the finish, while glycerol and gelatin enhanced it. Of the many alcohols and amides which have been tried subsequently, none has been more effective than glycerol from the standpoint of crispness, durability, and freedom from discoloration; the following sections relate to the utility of glycerol in this application.

TABLE V. EFFECT OF GLYCEROL AS A COREACTANT

Ratio *PAA*/glycerol	Cure (min.)	Cure (°F)	Stiffness Gurley (mg./in.) Unwashed	Stiffness Gurley (mg./in.) Washed	Stiffness retained (%)
10:0	10	350	19	16	84
10:1			19	13	68
10:3			22	23	105
10:10			22	17	77
10:30			21	17	81
10:0	0.33	400	19	12	63
10:1			17	15	88
10:3			15	17	113
10:10			11	23	209
10:30			20	56	280

Glycerol as a Coreactant

To show the effect of a polyacrylic acid/glycerol combination, swatches of nylon fabric were treated with 5% solids polyacrylic acid plus 0% to 15% glycerol. After drying and curing at either 350°F for 10 min. or 400°F for 20 sec., the fabrics were evaluated for durable stiffness as in the earlier study. Data are given in Table V.

Because of several apparently anomalous values, only a few conclusions can be drawn. The 10:3 ratio appears about optimum, in so far as 100%

stiffness retention is concerned. It is further evident that the glycerol has a peculiar effect on stiffness when added in large amounts; this will be discussed in a later section.

To show more completely the effect of glycerol as an adjunct to polyacrylic acid, the data of Table VI were obtained. Here a rate-of-cure study was made, employing in one case 5% (applied solids) *PAA*, and in the other 5% *PAA* plus 1½% glycerol.

It is obvious that the glycerol imparts greater durability at a given cure; there is also slightly greater crispness, which is not apparent from the Gurley values.

The effect of the glycerol may also be shown by means of weight-retention studies. In a comparison of polyacrylic acid, polyacrylic/glycerol 10:3, and polymethacrylic acid, approximately equal amounts of each material were applied to weighed nylon swatches, which were then cured, reweighed, scoured 40 min. at 180°F in 0.1% soap and 0.1% soda ash, dried, and reweighed. While no correction has been made for pickup of sodium ions from the wash liquor, it is very apparent from the data presented in Table VII that the glycerol increased the durability of the finish. The comparative lack of reactivity of polymethacrylic acid is also clearly indicated.

Glycerol Alone

Returning for a moment to the data of Table V, where a high glycerol content (*e.g.*, 10:30) and a severe cure caused a tremendous increase in stiffness on washing, subsequent experiments have shown this to be due to the action of the glycerol on the nylon under severe curing conditions. For example, if increasing amounts of glycerol are baked into a series of nylon fabrics, and the latter are subjected to stiffness tests before and after washing, data such as are shown in Table VIII will be obtained.

TABLE VI. EFFECT OF CURING TIME ON DURABILITY

Ratio *PAA*/glycerol	Cure (min. at 300°F)	Stiffness Gurley (mg./in.) Unwashed	Washed	Stiffness retained (%)
10:0	1	14	2	14
	5	16	3	19
	10	19	8	42
	15	17	9	53
	20	25	9	36
	30	19	12	63
10:3	1	10	2	20
	5	15	6	40
	10	17	11	65
	15	18	12	67
	20	21	23	109
	30	22	25	114

The concentration of glycerol must be high and the curing conditions quite severe before any appreciable effect is observed. Then, beyond a certain limit, there is a pronounced increase in stiffness, which is even further enhanced on washing. The action is possibly one of fusion of the nylon, similar in effect (but not in practicality) to the zinc chloride treatment reported by Mecklenburgh [3]. The increased stiffening on washing is probably due in part to the removal of glycerol, which would otherwise plasticize the stiffened fibers; this may not be the only factor, however, since the washfast stiffness values for *PAA* alone (*cf.* Table I) also tend to exceed 100% under severe curing conditions. Because the fabric tends to be overly embrittled, however, the use of glycerol alone has not been studied further.

It might be conjectured, in the light of the above, that the beneficial action of glycerol, when used in conjunction with polyacrylic acid, is due not only to the partial reaction of the glycerol with the acid but also to the ability of the glycerol to act as a "solvent medium" to facilitate the reaction of the acid with the nylon.

TABLE VII

Treatment	Cure	Cured wt. of size (g.)	Washed wt. of size (g.)	Retention (%)
PAA	10 min., 240°F	0.244	0.000	0
	10 min., 350°F	0.226	0.074	33
PAA/glycerol	10 min., 240°F	0.263	0.033	13
	10 min., 350°F	0.275	0.208	76
PMA	10 min., 240°F	0.205	0.003	1
	10 min., 350°F	0.220	0.019	9

TABLE VIII. EFFECT OF GLYCEROL, BAKED INTO NYLON FABRIC

Concentration (%)	Cure (min.)	Cure (°F)	Gurley stiffness Unwashed	Gurley stiffness Washed
5	10	350	2	—
	0.33	400	2	—
	0.16	425	5	1
10	10	350	3	—
	0.33	400	6	4
	0.16	425	6	6
15	10	350	3	9
	0.33	400	18	9
	0.16	425	24	89

Acidity of the Treated Fabric

Earlier it was shown (Table III) that there is a slight reduction in carboxyl content of the *PAA* on reaction with nylon. Similar studies of *PAA*/glycerol-treated nylon have shown only a slight additional reduction in free acid content due to the action of the glycerol. A *PAA*/glycerol-treated fabric which analyzed 4.20% *PAA* on drying showed 3.95% *PAA* after curing for 60 min. at 300°F.

Of greater practical value is a comparison of the pH of the treated fabric. A brief study was made on a 5% *PAA* treatment and a 5% *PAA*/1.5% glycerol treatment under the following conditions: a 2 in. × 2 in. section of each fabric, which had been cured 10 min. at 300°F, was cut into small bits and placed in 30 ml. of distilled water; pH measurements were made initially and after 5 min. and 15 min.; 5 ml. of 0.01*N* sodium hydroxide was then added, and pH was observed at intervals up to 140 hrs. Table IX lists the results.

It may be noted that the 10:3 finish has a slightly but consistently higher pH. The gradual drop in pH following the addition of alkali could indicate hydrolysis of ester or amide groups, or, more likely, penetration of the alkali into the difficultly swollen finish. This matter has not been studied further.

Practical Aspects

Durability of the Finish

The finish, if thoroughly cured, cannot be removed by boiling 0.1*N* NaOH or 0.1*N* HCl, by ordinary oxidizing or reducing treatments, or by solvent extraction. This unusual resistance makes for exceptional durability; on the other hand, it can become a disadvantage when it is desired to strip off the finish for reprocessing.

TABLE IX. pH OF TREATED FABRICS

Ratio *PAA*/glycerol	Fabric pH Initial	5 min.	15 min.	plus 5 ml. 0.01*N* NaOH 5 min.	15 min.	20 hrs.	140 hrs.
10:0	4.1	4.1	4.0	6.8	6.7	6.6	6.3
10:3	4.6	4.5	4.4	10.1	9.1	7.2	6.8

TABLE X. EFFECT OF THE *PAA* FINISH ON PHYSICAL PROPERTIES

Treatment (%) *PAA*	Treatment (%) Glycerol	Tensile strength (lbs.)	Trapezoid tear strength (lbs.)	T.B.L. abrasion (cycles)
—	—	50	12.0	14,000
1.0	—	53	8.7	20,000
2.5	—	54	8.5	42,000
5.0	—	53	7.7	60,000
1.0	0.3	49	9.7	26,000
2.5	0.75	49	7.3	47,000
5.0	1.5	53	7.2	85,000

The resistance of the finish to alkali is further shown by the fact that a *PAA*/glycerol-treated nylon fabric (cured 30 sec. at 425°F) retained 69% of its stiffness after immersion in 5% sodium hydroxide at room temperature for 24 days.

Concentration Required

The amount of polyacrylic acid required varies not only with the stiffness desired, but also with the type of fabric. As little as 0.1% solids gives a noticeable effect on taffeta; 0.5% solids are required on marquisette, and 1% or more may be needed to obtain threshold effects on spun nylon. Additional solids naturally impart greater stiffness. In this study, made on nylon taffeta, as much as 5% solids was applied in order to emphasize the effect and facilitate testing; this imparted a papery crispness. Subsequent tests at lower concentrations have shown that durability is not dependent so much on applied solids as on type of fabric, soft spun constructions showing greater washdown than filament fabrics.

Effect on Physical Properties

Table X lists tensile, trapezoid tear, and T.B.L.* abrasion data on a nylon fabric treated with several *PAA* formulations.

* Tootal Broadhurst Lee.

The over-all effect is about what would be expected from the application of a surface polymer to a textile fabric [1, 4]: tensile not appreciably affected; tear strength reduced; resistance to flat abrasion considerably increased.

Other Properties

When *PAA*-treated nylon is exposed to ultraviolet light, the tensile strength loss is neither greater nor less than would be observed with untreated nylon similarly exposed. The stiffness of the treated fabric is likewise unchanged, but the washfastness is somewhat reduced, depending on the duration of the exposure.

Because of the bonding of the yarns, a definite degree of antislip is imparted.

The *PAA*-treated nylon has no antistatic properties, either in the free-acid form or as the ammonium, sodium, or amine salt.

Change in the shade of dyed fabrics on *PAA* treatment varies with the dye, but ordinarily is not great. Lightfastness may be lessened or improved.

The treated fabric possesses cation-exchange properties, and will absorb basic dyes, metal ions, and similar materials.

Commercial Value

The chief advantage of the *PAA* treatment as a nylon finish is its durable crispness. The chief disadvantages, in all probability, lie in the fact that the treating solution is quite acid (pH 2 to 3) and that a severe cure is required. Since nylon can stand both the acidity and the cure, the problem is one of equipment and operating economy rather than fabric damage.

More to the point in evaluating a potential finish is a comparison with other methods of attaining the same or a similar result; certain urea and melamine resins can be utilized to provide satisfactory durable crispness with less acidity and a more normal cure.

Nevertheless, the *PAA* finish is being used commercially as a stiffener for nylon lace, and it merits consideration in other applications. The polyacid can, for example, be applied as warp size, and heat-set after weaving to obtain a fabric having an interesting unidirectional stiffness. The possibility of varying the coreactant should not be overlooked, either for loom finishing or for final finishing.

Summary

It has been shown that polyacrylic acid can be heat-set onto nylon to impart a very durable crisp finish, the durability being proportional to the severity of cure. Actual chemical combination between the polyacrylic acid and the nylon appears likely, although the reaction mechanism has not been elucidated. Addition of glycerol (or certain other materials) will increase the durability at a given cure. The ability of glycerol alone to stiffen nylon, under proper conditions, has been demonstrated. The properties of the polyacrylic acid-treated fabric have been outlined, and the commercial value discussed.

Neither the theoretical nor practical aspects have been fully explored in this brief study, which is presented in the hope of encouraging further consideration of the subject.

Acknowledgment

Credit is extended to Mrs. Betty Haffner for her aid in carrying out much of the experimental work.

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Properties of Apparel Wools

III. The Mechanical Behavior of Top and Roving Made on the French Worsted System *

Harris M. Burte†

Textile Research Institute, Princeton, New Jersey

Abstract

A description is given of the measurement of the tensile force-extension curves of fiber assemblies with no net twist—*i.e.*, top and roving produced on the French worsted system. Typical force-extension curves are presented, and the effects of testing conditions on various parameters of these curves have been determined. These force-extension curves are a measure of the forces required to cause the fibers to slip over one another; they depend on such factors as fiber length, fiber diameter, fiber modulus of elasticity, interfiber coefficient of friction, and fiber crimp, and on density of fiber packing in the assembly, fiber parallelism, and weight per unit length of the assembly. The relationships between the above factors and parameters of the force-extension curve are discussed in the light of the use of these measurements to investigate processes which affect any of these factors or to characterize different fiber types.

The variability of parameters of the force-extension curve is discussed. Part of the variability may be ascribed to slight differences in the performance of the machine units producing the assemblies.

Introduction

Low-twist fiber assemblies such as card sliver, top, and roving are produced during the processing of staple fibers into yarns. If a strand of such an assembly is tested in a tensile testing machine, using a gage length appreciably greater than the fiber staple length, fiber slippage rather than fiber breakage occurs as the strand is pulled apart. The mechanical properties determined in this test are a measure of the forces required to cause the fibers to slip over one another; they depend on such factors as fiber length, fiber diameter, fiber modulus of elasticity, interfiber coefficient of friction, and fiber crimp, and on density of fiber packing in the assembly, fiber parallelism, and weight per unit length of the assembly. Measurement of the mechanical properties of fiber assemblies is a useful method both of investigating processes which affect any of the above factors and of characterizing different fiber types.

The literature contains several applications of this method. Balls [2] compared thirteen cottons by measuring the mechanical properties of their rovings, and he discussed many of the factors which influence the mechanical properties. Moore [11] compared two cottons, measuring the mechanical properties of hand-carded slivers and of various assemblies through processing. Speakman and coworkers [14, 15] measured the mechanical properties of tops as an aid to their study of the oiling of wool; similar studies were made at the Wool Industries Research Association [3, 19]. Eckert and Hoffmann [5] compared fiber types by measuring the strength of carded webs. The effect of Syton on the strength of worsted slubbings was measured by Townend and Yu [16]. Lipowsky [10] investigated changes in fiber crimp and fiber parallelism by measuring the mechanical properties of slivers. Most of these workers considered only the maximum load which the assembly would support; some work done in Germany [12] made use of the entire force-extension curve. While the present paper was in preparation, Anderson, Cox, and Hardy [1] and Waggett [18] published further work on the force-extension curves of slivers.

* Parts I and II appeared in the February and July, 1952, issues of TEXTILE RESEARCH JOURNAL, respectively.

This work was conducted as part of the Wool Research Project sponsored by the American Wool Council, the International Wool Secretariat, the National Wool Trade Association, the United States Department of Agriculture, the Office of Naval Research of the Navy Department, and by a number of American wool manufacturers.

Part of the material reported in this paper was presented at a meeting of The Fiber Society, Swampscott, Mass., Sept. 1951.

† At present in the U. S. Air Force.

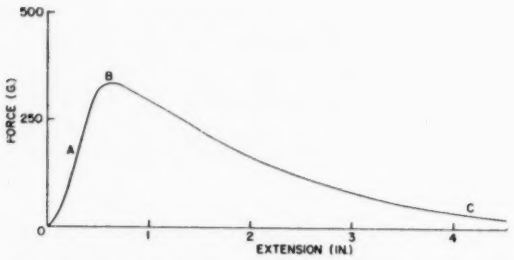

FIG. 1. *Typical force-extension curve for worsted top with no net twist. Gage length = 10 in.; rate of extension = 5 in./min.; 65% R.H., 70°F.*

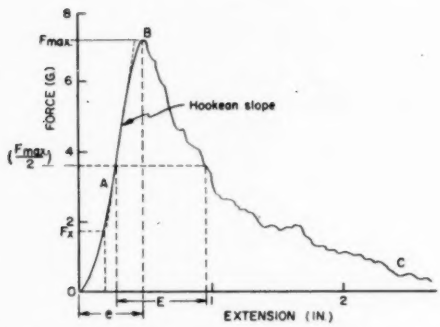

FIG. 2. *Typical force-extension curve for worsted roving with no net twist. Gage length = 15 in.; rate of extension = 5 in./min.; 65% R.H., 70°F.*

The present paper describes the measurement and interpretation of the tensile force-extension curves for top and roving produced on the French worsted system.* These assemblies have no net twist, and the effects of twist, such as that in a Bradford system roving, are not considered. The concepts developed should be applicable to assemblies (with no net twist) of any fiber type. Later papers in this series will describe the application of these measurements to the comparison of different wools and to a study of the aging of top and roving.

Measurement of the Force-Extension Curve

The force-extension curves (Figures 1 and 2) were measured using the Instron constant-rate-of-extension tensile testing machine [7]. Single-strand samples of the fiber assemblies were mounted between jaws with parallel plane faces; the gage length (initial distance between the jaws) was greater than the longest single-fiber length. All testing was done in a conditioned room where atmospheric humidity and temperature were controlled. It was found that a few hours' practice sufficed to train operators to use a standard mounting procedure which eliminated operator differences.

The two experimental precautions described below with specific reference to roving should be applicable to any low-twist fiber assembly which is wound into a ball or a bobbin.

(*a*) Figure 3A is a diagram showing the course of the winding of a roving strand on a bobbin. At the edge of the bobbin, where the direction of winding is reversed, the fibers in the roving strand are usually somewhat disarranged, as shown in Figure 3B. This disarrangement will affect the mechanical properties of the strand. It is best to choose samples which do not contain a section from the edge of the bobbin.

(*b*) During processing into roving the fibers may be deformed. For example, when the roving strand is wound onto the bobbin the fibers are laterally deformed, and the density of fiber packing in the roving is increased. When the strand of roving is removed from the bobbin the fibers can undergo recovery from these deformations, and their states of packing and crimp may change. Since such changes will affect the mechanical properties of the roving strand, it is necessary to standardize the time interval between removing the strand from the roving bobbin and testing it. (The subject of recovery of fibers which have been deformed during processing will be treated more fully in a later paper on the aging of top and roving.) In most of the experiments described in this paper the samples were mounted in the testing machine and extended within 1 min. after being removed from the bobbin.

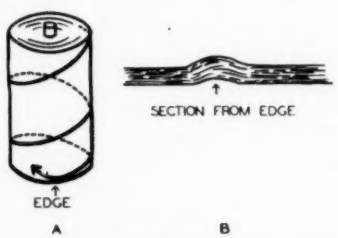

FIG. 3. *Disarrangement of fibers due to a reversal in the direction of winding the roving strand onto the bobbin.*

* The Wool Research Project was concerned with an evaluation of the properties and processing of four wools: an Australian 70's grade Merino, a New Zealand 58's grade crossbred, a U. S. 64's grade Rambouillet, and a U. S. 58's grade crossbred. A summary of the processing operations was given in the first paper of this series [17]. The weight per unit length of all tops was 20 g./m., that of all rovings was 0.208 g./m.

The Force-Extension Curve

Figures 1 and 2 present typical force-extension curves for top and roving.* The testing conditions given in the figure captions are those which had been chosen for applications of these measurements to studies of aging. The effects of varying testing conditions will be discussed in a later section (p. 473).

In the region O–A, extension of the assembly strand is primarily by deformation of the fiber crimp; little fiber slippage occurs. At B, the point of maximum load, fiber slippage predominates. Attenuation of the breaking zone causes further extension, B–C, to take place by fiber slippage in a localized section of the test length. As the number and length of fibers extending from one side of the break into the other decrease, the force necessary to maintain the constant rate of extension also decreases (see Appendix).

Some useful parameters of the force-extension curve are marked on the curve in Figure 2. The maximum load that the assembly will support, F_{max}, is measured at B.

The Hookean slope is defined as the steepest rate of increase of force in the region O–B of the curve. As extension of the assembly proceeds from O to A the slope of the force-extension curve usually increases, and the Hookean slope will largely depend on how far the curve OA can be developed (*i.e.*, how far the fiber crimp can be deformed) before fiber slippage becomes important. Therefore, for individual samples from a given roving, there should be a strong positive correlation between variations in the Hookean slope and in the maximum load (see Figure 13).

Another parameter characteristic of the early part of the force-extension curve is the force, F_x, at a given small extension (1% to 2% of the initial length).† This parameter, unlike the Hookean slope, does not have the disadvantage of a strong dependence on the maximum load.

The extension at the maxium load is designated as e. For some assemblies the initial slope of the force-extension curve is quite small, and it is difficult to define accurately the point O. Such difficulty may lead to relatively large errors in F_x and e.

The parameter E is a measure of the amount of fiber slippage that must take place for the load to decrease from the maximum load to $\frac{1}{2}$ the maximum load (see Appendix).

The area under the force-extension curve represents the energy needed to pull the sample apart. It is a composite parameter and is strongly influenced by the magnitudes of the Hookean slope, the maximum load, and E.

The Effect of Fiber Properties and Construction of the Assembly on the Force-Extension Curve

The use of mechanical properties of fiber assemblies to compare different fiber types or to investigate processes such as aging requires assumptions regarding the influence of factors such as fiber crimp or fiber length on the force-extension curves. Cox [4] presented an excellent discussion of various factors which affect the maximum load. This section continues such a discussion, and where it is possible presents assumptions about the influence of these factors on various parameters of the force-extension curve. Some of the assumptions are verified by data appearing in the literature [10, 16] and by the results of the experiments described in the next section. Experimental information is not extensive enough to verify all of the assumptions.

Interfiber Coefficient of Friction

Since little fiber slippage occurs in the region OA of the force-extension curve, this part of the curve, and consequently F_x, should be relatively insensitive to changes in the interfiber coefficient of friction. An increase in the coefficient of friction will increase the amount of deformation of the fiber crimp that must take place before slippage can occur, and should therefore increase e, the maximum load, and the Hookean slope. Townend and Yu [16] have shown that increasing the coefficient of friction by the application of Syton to the fibers will increase the maximum load.

Fiber Modulus of Elasticity

Since extension of the assembly up to the maximum load is primarily by deformation of the fiber crimp, an increase in the modulus of elasticity should increase F_x, the Hookean slope, and the maximum load. The parameters E and e should be relatively insensitive to changes in the modulus of elasticity.

Weight per Unit Length of the Assembly

For a given fiber diameter, an increase in the weight per unit length of the assembly will, by increasing the number of fibers in the cross section, increase the

* See footnote, p. 470.

† In this paper extension in percent units refers to a percentage of the initial length.

number of fiber contacts at which slippage must occur for the assembly to be extended. (The crimped wool fibers in the assembly will tend to have points of contact rather than areas of contact [4].) The result should be an increase of F_x, of the Hookean slope, and of the maximum load; e and E should not be affected.

Fiber Diameter

For an assembly with a given weight per unit length, an increase in fiber diameter will decrease the number of fibers in the cross section and will increase the force needed to deform the fibers at each point of contact. These two effects may not cancel one another; any decrease in the number of fibers in the cross section should cause a more than proportionate decrease in the number of fiber contacts, since there will be an increase in the fraction of possible points of contact which are ineffective by reason of being on the outside surface of the assembly. The net effect may be a decrease in the maximum load with increase of fiber diameter.

Fiber Length

Changes in the fiber staple length should not affect the region, OA, of the force-extension curve where fiber slippage is negligible. An increase in fiber length should increase the maximum load, the Hookean slope, e, and E, by increasing the length for contact of the individual fibers (see Appendix).

Density of Fiber Packing

An increase in the density of fiber packing in the assembly will increase the number and degree of contact of the fiber contacts that must slip over one another for the assembly to be extended, and should increase the maximum load and the Hookean slope.

Fiber Parallelism

For a given fiber crimp and density of fiber packing, an increase in fiber parallelism should tend to increase the number of points of contact that any one fiber makes with its neighbors. However, the axial load on the assembly strand can be resolved into two components, one pressing the fibers together and one causing the fibers to slip over one another; an increase in the parallelism of the fibers should decrease the former and increase the latter. Furthermore, the decrease in the wandering of fibers from the inside to the outside of the assembly caused by the increase in the degree of parallelism will increase the possibility of slip planes being set up so that fibers may move in clusters rather than individually. The net effect of increasing fiber parallelism is probably a decrease in the maximum load. Some experiments by Lipowsky [10] tend to confirm this argument.

Fiber Crimp

For assemblies of crimped fibers, the crimps provide the points of contact that must be deformed and that must move past one another when fiber slippage occurs. In general, an increase in fiber crimp will tend to increase the maximum load and e, and will tend to decrease the rate of increase of force in the early regions of the force-extension curve (decrease F_x). However, predictions of the effect of fiber crimp are complicated both by the many different types of crimp that can exist, and, especially for natural fibers, by the difficulty of defining the crimp. Several idealized types of fiber crimp are depicted in Figure 4.

Consider the simple types of crimp where the amplitude and wave length of the crimp are very small compared to the fiber length (Figure 4 (a, b, c, d)). For the same degree of fiber parallelism and density of fiber packing, an increase in the crimp amplitude (a to c) or the crimp frequency (a to d) should increase the maximum load and decrease F_x. The shape of the crimps will also be important; an assembly containing fibers of crimp type (a) should have a higher maximum load than one with fibers of crimp type (b).

Crimp such as (e) will be accompanied by poor fiber parallelism. It is possible to have a combination of crimp types (a) and (e) as in type (f). A comparison of the maximum loads of assemblies with fibers of crimp types (a) and (f) should be similar to the comparison of assemblies with high and low degrees of fiber parallelism. For crimp types (e) or (f), F_x should be less than for crimp type (a).

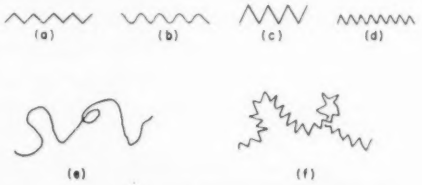

FIG. 4. *Several types of fiber crimp.*

TABLE I. THE EFFECT OF RECOVERY TIME ON THE TENSILE RECOVERY OF ROVING (INITIAL EXTENSION = 3.04%)

Time (min.)	Recovery/extension
0	0.78
1	0.85
108	0.94
263	0.94

As with the other fiber properties, this discussion of crimp has considered the crimp of the fibers in the assembly rather than the crimp of the fibers before they are processed into the assembly. An assembly made from highly crimped fibers will tend to have a lower density of fiber packing and perhaps a lower degree of fiber parallelism than an assembly made in the same way from fibers with relatively little crimp. Interrelationships of this nature must be considered when interpreting experimental results.

Some Experimental Results

The following experiments on worsted rovings with no net twist were performed to investigate the effects of varying testing conditions, and to obtain information regarding some of the assumptions in the preceding section. With the exception of the experiment on the effect of relative humidity, all mechanical properties were measured on samples preconditioned to and tested at 65% R.H. and 70°F.

Tensile Recovery

Samples of roving were extended various amounts at a constant rate of extension of 5 in./min. and were immediately allowed to contract at the same rate. Figure 5 shows some typical force-extension curves where the samples were re-extended to break immediately after the first cycle. The experimental results are summarized in Figure 6; both recovery and initial extension are expressed as a percentage of the initial length. In another experiment the samples were allowed to rest at no load before re-extending. An example of the effect of this additional recovery time on the ratio of recovery to initial extension is given in Table I.

For small extensions in the region *OA* of the force-extension curve (Figure 2) almost all of the initial extension is recoverable. This verifies (for the rapid rate of extension of 5 in./min.) the previous statement that, in this region of the curve, extension of the assembly is by deformation of fiber crimp rather than by fiber slippage. As extension proceeds from *B* to *C* and the force decreases, deformation extension is converted into slippage extension; thus, the amount of recovery decreases.

Orientation of Fibers in the Broken End

It was observed that, when a sample of roving is pulled apart, the fibers on either side of the break tend to be oriented with their tip ends pointing toward the break. This is evidence that the interfiber coefficient of friction must influence the force-extension curve.

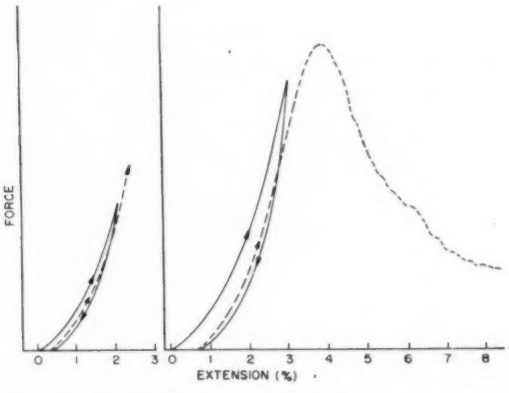

FIG. 5. *Extension-contraction cycles for strands of roving; ——, first extension-contraction cycle; – – –, second extension.*

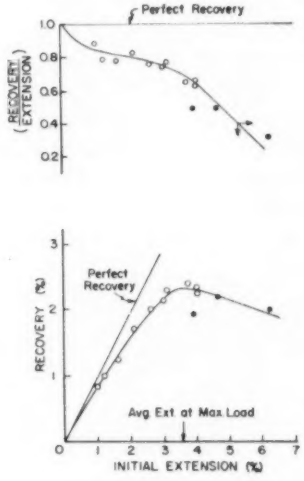

FIG. 6. *Tensile recovery of roving.* ●*—Samples where the initial extension was well beyond the maximum load.*

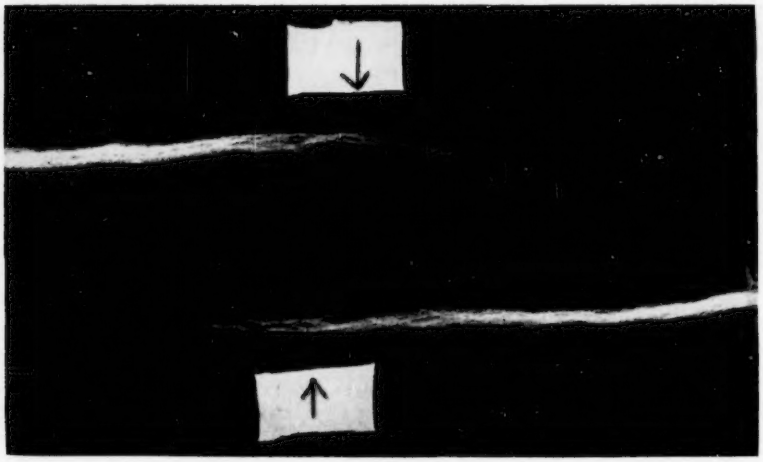

FIG. 7. *Typical section at which the orientation of the fibers was noted.*

In order to investigate this effect, the ends of broken rovings were examined. The breaks were effected manually on lengths greater than 30 in. Breaks which occurred near a grip were discarded since fiber orientation at the break could, in such cases, be affected by the gripping rather than the slipping of the fibers. Figure 7 shows a typical break and a typical section at which the orientation of the fibers was noted. The results given in Table II are the sums for twenty such samples. Also given are the results from four samples of undisturbed roving which were cut with a razor blade; these samples serve as a control.

It is well known (see, for example, [9]) that for normal wool fibers the coefficient of friction in the direction of the tip-to-root (anti-scale) is greater than that in the direction of the root-to-tip (with-scale). When the roving is pulled apart, the fibers should, other things being equal, tend to move in that direction for which the coefficient of friction is less. The observed orientation, where a majority of the fibers have their tip ends pointing toward the break, must therefore result.

TABLE II. ORIENTATION OF FIBERS IN THE BROKEN ENDS OF ROVINGS

	No. of fibers with tip ends toward break	No. of fibers with root ends toward break
Samples pulled apart	699	477
Samples cut (control)	560	570

Rate of Extension

The influence of the rate of extension on various parameters of the force-extension curve is summarized in Figure 8, the data having been obtained from 15-in. gage length samples of roving extended at constant rates of extension varying from 0.02 in./min. to 20.0 in./min. The increase in maximum load with increase of rate of extension is in agreement with results reported by Cox [4], who ascribed this behavior to the effect of rate of extension on the modulus of elasticity for deformation of fiber crimps.

In general, the force-extension curve is relatively insensitive to rate of extension. Greater rates of extension have the advantage of decreasing the time

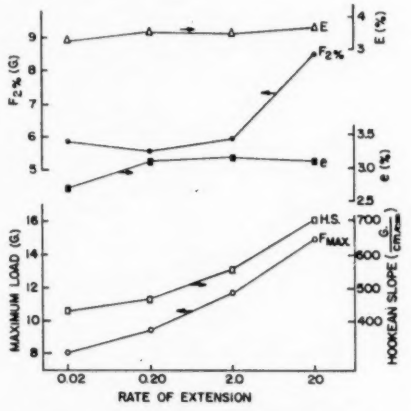

FIG. 8. *The effect of rate of extension on various parameters of the force-extension curve for roving.*

needed for testing but, since they increase the rate of change of the force, they decrease the sensitivity with which the testing machine can measure the force. Using the Instron Tensile Tester, the fastest convenient rate of extension for these experiments was 5 in./min., and this was chosen as a standard for the other experimental work described in this paper.

Gage Length

The effect of gage length was studied on roving samples of three different gage lengths extended at a constant rate of extension of 5 in./min. The gage lengths chosen were as follows:

(*a*) 7 in.—This was the shortest gage length with which there was no possibility of some long fibers being gripped by both jaws.

(*b*) 15 in.—For the size of roving bobbin and type of winding used, this was the longest convenient gage length which would not necessitate the inclusion in the test length of a section from the edge of the roving bobbin (see Figure 3).

(*c*) 25 in.—This was the longest gage length that could be used on the Instron Tensile Tester.

Since extension of the roving after the maximum load takes place primarily in a localized section, the rate of extension was kept the same for the three gage lengths. The effect of gage length on various parameters of the force-extension curve is summarized in Figure 9.

With a 7-in. gage length many of the fibers in the broken end are gripped in one or the other of the jaws, and these fibers must move in the direction dictated by the jaw motion rather than in the manner which will require least force. Thus, the maximum load for a 7-in. gage length is greater than that for a 15-in. gage length. That for a 25-in. gage length is slightly less than that for the 15-in. gage length for several reasons: (*a*) the effect of the section from the edge of the bobbin; (*b*) the greater probability of encountering a weak place; (*c*) the greater probability of nonlocalized fiber slippage.

The Hookean slope is expressed both as

$$\left(\frac{\text{g.}}{\text{cm. extended/gage length}}\right)$$

and as (g./cm. extended). The dependence of the former parameter on gage length is similar to that of the maximum load, and is due to the dependence of the Hookean slope on the maximum load. The much stronger dependence of the latter parameter on gage length, as well as the constancy of e when expressed as a percentage of the gage length, indicates that extension up to the maximum load is of the whole test length rather than of a localized section.

The increase in E at very long gage lengths may be due to larger amounts of nonlocalized fiber slippage that can occur before the maximum load is reached. E is not expressed as a percentage of the initial length because even with this nonlocalized fiber slippage it is primarily a property of the localized section where the break occurs.

The slight dependence of $F_{2\%}$ on the gage length may be due to the use of plane-faced jaws which cause some deformation of the roving strand at the jaws. It would be expected that this deformation affects primarily the early region of the force-extension curve, and the relative effect of this deformation should be greater for the shorter samples.

For the other roving testing described in this paper a standard gage length of 15 in. was chosen (the average fiber staple length in all rovings tested was

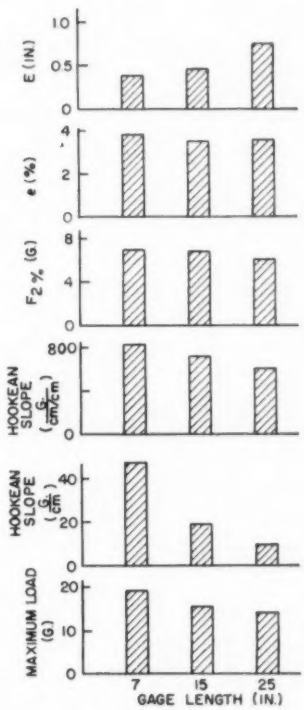

FIG. 9. *The effect of gage length on various parameters of the force-extension curve for roving.*

TABLE III. EFFECT OF LOCATION OF BREAKING ZONE ON THE MECHANICAL PROPERTIES OF ROVING

Parameter of force-extension curve (arbitrary units)	None of the fibers participating in the break gripped by jaws	Many fibers in one broken end gripped by jaws
Maximum load	12.8	12.3
Hookean slope	5.53	5.39
E	1.03	1.10
e	1.04	1.04

between 2.4 and 3.4 in.). With this gage length the localized sections at which break occurred seemed to be randomly distributed along the test lengths. Furthermore, the data in Table III indicate that there was no difference in the mechanical properties between samples which had the fibers in *one* of the broken ends gripped by one of the jaws and those where none of the fibers participating in the break were gripped by one of the jaws.

Relative Humidity

The results of a series of tests on samples of roving from bobbins which had been conditioned at three relative humidities are presented in Figure 10. In another experiment a bobbin of roving was equilibrated at 85% R.H., and was then placed in an atmosphere at 65% R.H. Samples were tested after various times in the latter atmosphere, and the results presented in Figure 11 show the changes that occur in parameters of the force-extension curve as the roving goes from a regain corresponding to 85% R.H. to one corresponding to 65% R.H.

The crimped wool fibers in the roving tend to have points of contact rather than areas of contact [4]. Consider a greatly simplified diagram (Figure 12) of the fibers at one such point of contact. The arrows represent the direction of motion of the fibers. The axial load, F, on the strand can be resolved into two components: $F \cos \theta$, the force available to overcome friction at the point of contact, and $F \sin \theta$, a normal force pressing the fibers together at the point of contact. In a very elementary way it can be said that for slippage to occur the fibers must be deformed at the point of contact from the original contact angle θ_o to θ_s such that

$$F\ (\cos \theta_s) = \mu F\ (\sin \theta_s),$$

μ being the coefficient of friction. Thus, for slippage to occur, $\cot \theta_s = \mu$. Therefore, as μ increases, the amount of deformation needed for slippage to occur also increases.

It is well known that as the regain of wool fibers increases, the modulus of elasticity decreases [13],

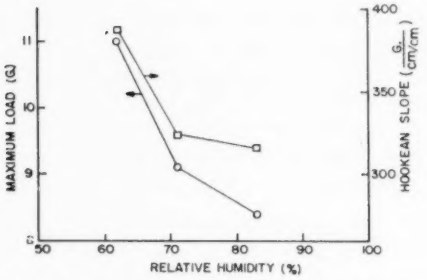

FIG. 10. *The effect of relative humidity on various parameters of the force-extension curve for roving.*

and there is evidence that as the regain increases, the coefficient of friction increases [8]. Therefore, as the regain increases, the higher resultant coefficient of friction requires that the roving be extended farther before slippage occurs (e increases), but the lower modulus of elasticity may allow a smaller force to perform this deformation (F_{max} decreases). F_x and the Hookean slope decrease due to the lower modulus of elasticity. There is no explanation at present for the change in E.

There is, however, another possible explanation of the effect of regain of the fibers on the force-extension curve of the roving. It has already been stated that in the process of unwinding a sample from

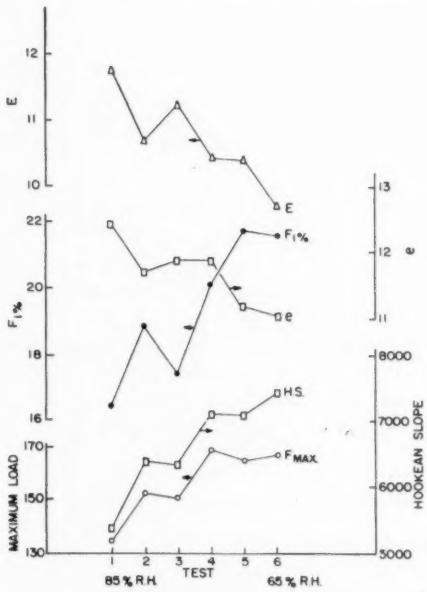

FIG. 11. *The effect of relative humidity on various parameters of the force-extension curve for roving. All parameters are expressed in arbitrary units.*

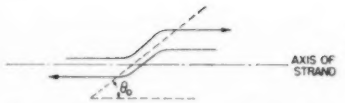

FIG. 12. *Point of contact between two fibers slipping over one another.*

the roving bobbin and inserting it in the jaws of the testing machine, the fibers in the roving can undergo recovery from previous deformations. There is the possibility that greater amounts of such an unwinding recovery will occur at the higher regains even though the bobbins of roving were preaged to inhibit the recovery. In a subsequent paper on aging, the effects of such a recovery will be discussed, and they are similar to those obtained in this experiment.

The Correlation Between the Hookean Slope and the Maximum Load

It was mentioned earlier that, for the assemblies investigated, the Hookean slope depends both on the the rate at which the force increases in the early regions of the curve and on the maximum load. The dependence of Hookean slope on maximum load can be obtained from the sample-to-sample variation in a given type of roving, as in Figure 13, and comparison of the Hookean slopes at comparable maximum loads leaves only the effect of the early region of the force-extension curve. For the example given in Figure 13, the change of the crimp (Figure 4) from type (a) or (b) to type (e) or (f) affected the Hookean slope by decreasing the rate at which the force increases in the early region of the curve, and by increasing the maximum load. Thus, while the average Hookean slopes for these two rovings differed by 35%, the Hookean slopes at comparable maximum loads differed by 46%.

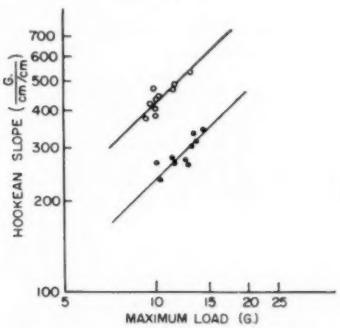

FIG. 13. *The dependence of the Hookean slope on the maximum load for roving.* ○—*Fibers having crimp type* (a) *or* (b) *of Figure 4.* ●—*Fibers having crimp type* (e) *or* (f) *of Figure 4.*

Experimental Variances

The variance of mechanical properties of samples from a single assembly strand or from strands produced on different machine units of the same processing step depends, of course, upon the type of processing equipment used. This section discusses such variance for one fiber assembly, roving, produced in a single mill using the French worsted system.* The discussion will be confined to one parameter of the force-extension curve, the maximum load. The results may not be directly applicable to the fiber assemblies produced at other stages in processing, to other mills, or to other processing systems, but they should indicate the types of variability to be expected.

The coefficient of variation of the maximum load for samples taken from closely adjacent positions along a single roving strand lies between 10% and 15%. Several factors may contribute to this variance:

(*a*) Variations in the weight per unit length (averaged over the whole gage length) of the samples. For the rovings tested the maximum load showed some dependence on the weight per unit length, but the correlation coefficient was only 0.30** (139 degrees of freedom), and this factor does not contribute very greatly to the over-all variability of the maximum load.

(*b*) The natural staple length distribution. This will lead to variations in the number of fiber-to-fiber contacts in the localized breaking zone (variations in the length for contact (see Appendix)).

(*c*) Variability in the density of fiber packing or in the fiber parallelism due to machine operation.

(*d*) The occurrence in the roving strand of thin spots or other weak places, the lengths of which are less than the gage length.

Long-period variability along the roving strand (possibly due to changes in atmospheric conditions during processing) may cause an increase in the coefficient of variation. Of greater importance are the differences in properties of strands produced from different sides of the same double-meche head, from different heads on the same roving frame, and from different roving frames. Figure 14 illustrates the differences that can exist between the two strands from one double-meche head, between heads, and between frames. The standard deviation shown is that for samples from a single strand; five samples were tested from each strand. Figure 15 presents

* See footnote, p. 470.

data which illustrate the lack of correlation between the average maximum loads for different strands and the average weights per unit length of these strands of roving. Therefore, the differences in mechanical properties cannot be ascribed to differences in weight per unit length among the various strands. It would seem that the differences in mechanical properties are caused by slight differences in the degree of fiber parallelism or in the density of fiber packing in the rovings produced by different machine units. For example, the rub apron on one head may be worn more than that on another head and would therefore be less efficient in condensing the roving.

Data for the roving strands from both sides (R and L) of several double-meche heads (H) on three frames (F) are presented in Table IV. The properties of the strands differ widely. However, when yarns are spun from these rovings the properties of all the yarns are quite similar; these data thus indicate that the differences in properties of the roving strands are not reflected in comparable differences in properties of the yarns spun from these rovings. The roving measurements are highly sensitive to small differences in fiber parallelism and fiber packing, a condition which does not obtain in highly twisted yarns whose properties depend more on the behavior of the single fibers themselves than on fiber interrelationships. It is possible, however, that the differences between roving strands indicated by the differences in their mechanical properties will cause the strands to have different spinnabilities.

The machine differences just described are an important factor in the design of an experiment to compare the roving properties of different wools. It is proposed that a useful experimental design is to process half of each wool in parallel, each on half of the available equipment. The wool-machine relationships are then reversed; the second half of wool A is processed on the machinery which processed the first half of wool B, and the second half of wool B is processed on the machinery which processed the first half of wool A. In this way any machine differences can be detected and eliminated from the comparison between the wools, and both wools are processed at the same time under similar atmospheric conditions.

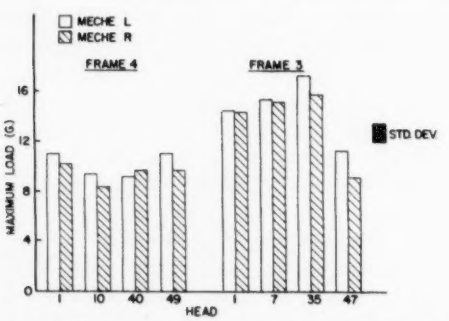

FIG. 14. *Differences in mechanical properties of rovings produced by different machine units.*

TABLE IV. YARN SPUN FROM IDENTIFIED STRANDS OF ROVING—MAXIMUM LOAD (RELATIVE TO $F_1H_{15}R$)

Frame and Head	F_1H_{15}		F_1H_{40}		F_2H_1		F_3H_{15}	
Meche	R	L	R	L	R	L	R	L
Roving	1.00	1.23	1.22	1.31	1.56	1.64	1.19	1.27
Yarn	1.00	0.98	0.96	1.00	1.00	0.93	0.94	0.93

Summary

The tensile force-extension curves for tops and rovings with no net twist have been measured with the Instron Tensile Tester using gage lengths appreciably greater than the fiber staple length. Initial extension of the assembly strand is primarily by deformation of the existing fiber crimp; little fiber slippage occurs. Extension beyond the maximum load is primarily by fiber slippage in a localized section, without fiber breakage, until the assembly strand is completely pulled apart.

Among the useful parameters of the force-extension curve are the force at a fixed low extension, the steepest rate of increase of force in the initial portion of the curve, the maximum load, and the extension at the maximum load. The effects on these parameters of variations in such testing conditions as rate of extension, gage length, and relative humidity are described.

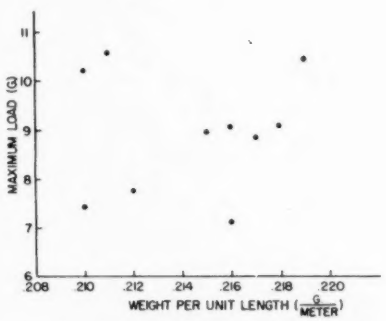

FIG. 15. *Data illustrating the lack of correlation between the mechanical properties of roving strands produced by different machine units and the weights per unit length of these strands.*

The force-extension curve is influenced by such factors as fiber length, fiber diameter, weight per unit length of the assembly, fiber modulus of elasticity, interfiber coefficient of friction, fiber crimp, fiber parallelism, and density of fiber packing in the assembly, and the relationships between these factors and various parameters of the curve are discussed. Measurement of the mechanical properties of fiber assemblies should be a useful method both of investigating processes which affect any of the above factors and of characterizing different fiber types.

The variances of mechanical properties of samples from a single assembly strand or from strands produced on different machine units of the same processing step are discussed for roving produced on the French worsted system. The differences between the roving strands produced by different machine units do not seem to be reflected in comparable differences in properties of the yarns spun from these rovings.

Appendix

This appendix presents an attempt to derive an expression for the descending portion of the force-extension curve. The recent paper of Anderson, Cox, and Hardy [1] also had a theoretical treatment of this portion of the force-extension curve.

It will be assumed that extension of the assembly strand up to the maximum load can be attributed entirely to deformation of the crimp, and that, if the force is decreased, this deformation is quickly recoverable. Data presented in a previous section (p. 473) indicate that this assumption is sufficiently valid to be useful. Further assume that all fibers have the same diameter, are parallel to the long axis of the strand, and do not have a differential coefficient of friction. Since most of the fiber slippage occurs in a localized section, it will be assumed that only those fibers which cross a given plane Z–Z, perpendicular to the long axis of the strand (see Figure 16a), need be considered. The position of such fibers with respect to Z–Z will determine their direction of motion. The net slippage of any fiber is assumed to be along the fiber axis and to be equal in direction and amount to the motion of the side of the break with which the fiber remains.

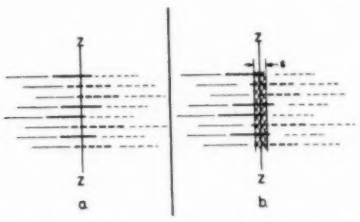

FIG. 16. *Idealized representation of fibers in assembly strand:* (a) *in undisturbed assembly strand;* (b) *after an amount of slippage extension equal to* S. ——, *Fibers that move with left-hand section.* – – –, *Fibers that move with right-hand section.*

Let n be the number of right-hand ends of fibers per unit length of the assembly, l be the length of any fiber, and $\phi(l)$ be the staple length distribution function which is normalized as

$$\int_0^\infty \phi(l)\, dl = 1. \tag{1}$$

As was shown by Foster, Gregory, and Wormersly [6], the number of fibers (dN_l) of lengths l to $l + dl$ which cross Z–Z is

$$dN_l = nl\,\phi(l)\, dl, \tag{2}$$

and it can be shown that the number of fibers (dN_{lX}) of lengths l to $l + dl$ which cross Z–Z and have their right-hand ends in the interval extending from X to $X + dX$ to the right is

$$dN_{lX} = n\phi(l)\, dl\, dX. \tag{3}$$

It is now assumed that a fiber will move with the section on the left-hand side of the break if X is less than $l/2$. Such a fiber will move relative to the fibers in the right-hand section (slip over them), and in the unextended roving will have a length for contact with fibers over which it must slip equal to X. Since the two sides of the break can be considered as symmetrical, the total original length for contact (L_o) will be

$$L_o = 2n \int_{l=0}^{l=\infty} \int_{X=0}^{X=l/2} X\phi(l)\, dl\, dX. \tag{4}$$

The force necessary to cause the fibers to slip over one another will be assumed proportional to this total length for contact.

Consider now that part of the total extension of the assembly that is due to fiber slippage. Figure 16b shows the positions of the fibers with respect to the original plane Z–Z after a slippage extension S has occurred. Neglecting fiber contacts in the cross-hatched region of Figure 16b, the length for contact, with the right-hand section, of a fiber moving towards the left will be $(X - S)$. The total remaining length for contact after an extension S will be

$$L_S = 2n \int_{l=2S}^{l=\infty} \int_{X=S}^{X=l/2} (X - S)\phi(l)\, dl\, dX. \tag{5}$$

Note that when $S = 0$, equation (5) reduces to equation (4).

Performing the first integration:

$$L_S = n/4 \int_{2S}^{z} (l - 2S)^2 \phi(l)\, dl. \qquad (6)$$

Since the force necessary to cause the fibers to slip over one another has been assumed proportional to the length for contact,

$$\frac{F_S}{F_{max}} = \frac{L_S}{L_o} = \frac{\int_{2S}^{z} (l - 2S)^2 \phi(l)\, dl}{\int_{0}^{z} l^2 \phi(l)\, dl}, \qquad (7)$$

where F_{max} is the maximum load and F_S is the force after an amount of slippage extension S has occurred.

Since extension in the region OB of the force-extension curve (Figure 2) has been assumed as completely recoverable, the slippage extension should be measured as the distance along the abscissa between the ascending and descending portions of the force-extension curve. For example, E (Figure 2) is the slippage extension for the special case where $F_S/F_{max} = 1/2$.

If the staple length distribution for the fibers in an assembly is known, equation (7) can be used to calculate the descending portion, BC, of the force-extension curve. A comparison between experimentally observed and calculated curves is given in Figure 17.

Considering the extent of the simplifying assumptions, the agreement between the experimental and calculated curves is fairly good. If the length for contact in the cross-hatched region of Figure 16b is not neglected, the load for any given slippage extension will be greater than calculated. At very high extensions the attenuated breaking zone becomes spread out, and the rate of decrease of force is not as great as indicated in equation (7). These corrections would bring the experimental and calculated curves into better agreement.

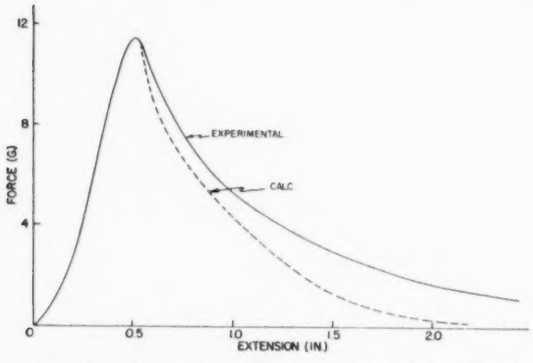

FIG. 17. *Comparison between an experimentally observed force-extension curve for roving and the curve calculated from equation (7). Roving made from the U. S. medium wool.*

Acknowledgment

The author wishes to thank Prof. J. C. Whitwell and Dr. J. H. Wakelin for their discussions and assistance in clarifying the presentation. He would also like to acknowledge the assistance of Miss Dorothy O'Reilly in the experiment on the orientation of fibers in the broken ends of rovings.

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Mechanical Properties of Cotton Fibers

Part II: Effect of Acids on Fibers under Tension*

J. A. Lasater,† E. L. Nimer,‡ and H. Eyring**

The Institute for the Study of Rate Processes, University of Utah, Salt Lake City, Utah

IN Part I of this series [7] it was noted that the relaxation constants obtained from the subsequent curves were the same as those from the initial force-relaxation curves (at constant elongation) for single cotton fibers. This provides the basis for a method of measuring quantitatively the effect of chemicals on cotton fibers. Using this characteristic behavior, a study of the reaction of the strong acids—hydrochloric, sulfuric, and nitric—with the fiber was conducted. These reactions are of interest, since it is well known that the *beta*-glucosidic linkages of cellulose are hydrolyzed by even dilute acid solutions.

Experimental

The instrument and technique used to obtain the initial relaxation curve for the water-saturated fiber were identical with those reported in Part I [7]. After the initial relaxation curve had been obtained, the water was removed and the acid solution pipetted into the test chamber. When the time rate of change of the curve was of the same order as that for the slow relaxation constant of the water-saturated fiber, the fiber was re-elongated to secure the relaxation curve in the test solution. The investigations were conducted on a seed cotton sample from the same stock as used in the previous work.

Results

The effect of the acid reagents has been divided into three categories. The acid relaxation curve was analyzed with the equation that described the relaxation curve of the fibers in air and water [7]:

$$F = C_1 e^{-\gamma_1 t} + C_2 e^{-\gamma_2 t}. \qquad (1)$$

In addition to affecting the relaxation constants of the fiber, the acid solutions caused an "instantaneous relaxation" of a portion of the force supported by the fiber whenever the acid concentration was above a critical minimum. This critical minimum concentration was a function of the temperature and the type of acid used.

The instantaneous relaxation of the force occurred as rapidly as the solution could be added to the reaction chamber, and appeared to occur throughout the entire length of the fiber. Undoubtedly, there is a finite time required for this effect to take place, but it was impossible to determine this time interval with the present experimental arrangement. The amount of the instantaneous relaxation was a function of the force supported by the fiber just prior to the application of the test solution and not a function of the initial force on the fiber at the beginning of the relaxation. The amount of instantaneous force reduction divided by the force on the fiber just prior to the addition of the acid has been designated as the "force reduction" ($\Delta f/f$). The various values obtained at one concentration and temperature check within $\pm 1\%$. The force reduction and the relaxation constants for the water-saturated seed cotton fibers treated with various concentrations of hydrochloric, sulfuric, and nitric acids are given in Tables I, II, and III, respectively.

The graphical representations of the variation of the force reduction with concentration and temperature for the three acids are shown in Figures 1, 2, and 3. When the force reduction is related to the hydrogen ion activity of the acid, as shown in Figures 4 and 5 for hydrochloric and sulfuric acids, the force reduction tends to approach a limiting value. The data for nitric acid suggest that the

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† Present address: Field Research Laboratories, Magnolia Petroleum Co., Dallas, Texas.

‡ Present address: California Research Corporation, Richmond, California.

** Dean of the Graduate School, University of Utah.

TABLE I. EFFECT OF HYDROCHLORIC ACID ON WATER-SATURATED SEED COTTON FIBERS UNDER TENSION

Concentration (mols/1000 g. H_2O)	0°C			20°C			40°C			60°C
	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)
0 (water)	—	1.04	0.471	—	1.18	1.61	—	1.23	2.48	—
0.5	0	1.05	3.49	0	1.19	6.24	0	1.24	8.20	0
1.0	0	1.06	5.31	2	1.20	7.84	4	1.25	11.2	7
2.0	1	1.07	6.61	5	1.21	10.1	6	1.26	14.1	10
4.0	10	1.08	7.67	13	1.22	11.9	16	1.28	16.9	21
6.0	16	1.09	8.01	20	1.24	12.5	24	—	—	28

TABLE II. EFFECT OF SULFURIC ACID ON WATER-SATURATED SEED COTTON FIBERS UNDER TENSION

Concentration (mols/1000 g. H_2O)	0°C			20°C			40°C			60°C
	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)
0 (water)	0	1.04	0.471	—	1.18	1.61	—	1.23	2.48	—
0.5	0	1.05	3.94	0	1.19	5.78	—	1.24	6.41	10
1.0	0	1.06	5.31	2	1.20	7.84	10	1.25	8.72	20
2.0	0	1.07	6.06	6	1.21	9.75	19	1.26	11.7	28
4.0	3	1.12	7.32	15	1.25	11.5	27	1.28	14.6	38
6.0	10	1.15	7.84	26	1.27	12.5	37	—	—	45

TABLE III. EFFECT OF NITRIC ACID ON WATER-SATURATED SEED COTTON FIBERS UNDER TENSION

Concentration (mols/1000 g. H_2O)	0°C			20°C			40°C		60°C
	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)	$\Delta f/f$ (%)	$r_f \times 10^2$ (sec.$^{-1}$)	$r_s \times 10^5$ (sec.$^{-1}$)
0 (water)	—	1.04	0.471	—	1.18	1.61	—	1.23	2.48
0.5	0	1.13	4.73	3	1.25	6.06	6	1.34	10.1
1.0	0	1.18	5.69	6	1.29	8.01	19	1.39	12.2
2.0	0	1.24	6.79	12	1.31	10.4	27	1.45	13.8
4.0	3	1.31	8.50	25	1.43	12.2	37	1.53	15.7
6.0	14	1.34	9.35	36	1.48	13.5	46	—	—

same behavior would be found in this case also, but, unfortunately, supplementary activity data for nitric acid are not available. All activity data were obtained from Harned and Owens [6].

It is apparent that the acids react with the fiber to cause the force reduction. A logical explanation of this phenomenon is that acid reacts with some of the bonds that support the force. The nature of the reagents and the rapidity of the reaction suggest that the bonds that are attacked by the acid are hydrogen bonds. Thus, a reaction may be written:

$$\text{bond} + H^+ \underset{}{\overset{K'}{\rightleftharpoons}} \text{bond}\cdot H^+, \qquad (A)$$

where bond·H$^+$ represents the bond that has been attacked by the acid. This reaction was treated as a pseudo-equilibrium, with the equilibrium constant defined by

$$K' = \frac{(\text{bond}\cdot H^+)}{(\text{bond})\,(H^+)}. \qquad (2)$$

TABLE IV. PSEUDO-EQUILIBRIUM CONSTANTS FOR HYDROCHLORIC AND SULFURIC ACIDS ON WATER-SATURATED SEED COTTON FIBERS

Temperature (°C)	K'	
	Hydrochloric acid	Sulfuric acid
0	0.058	0.13
20	0.064	0.70
40	0.070	1.56
60	0.076	2.35

To evaluate this pseudo-equilibrium, it was assumed that the limiting value of the force reduction is proportional to the total number of bonds that can react with the acid in this manner, and the observed force reduction is proportional to the number of bonds that reacted. Using these assumptions, the pseudo-equilibrium constant is given by

$$K' = \frac{(\Delta f/f)}{[(\Delta f/f)_{\text{lim}} - (\Delta f/f)](H^+)}. \qquad (3)$$

The pseudo-equilibrium constants for the reaction

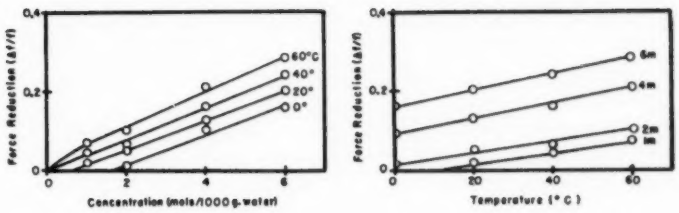

FIG. 1. *Instantaneous effect of hydrochloric acid on water-saturated seed cotton.*

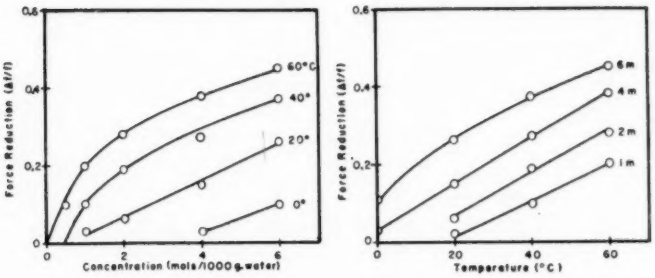

FIG. 2. *Instantaneous effect of sulfuric acid on water-saturated seed cotton.*

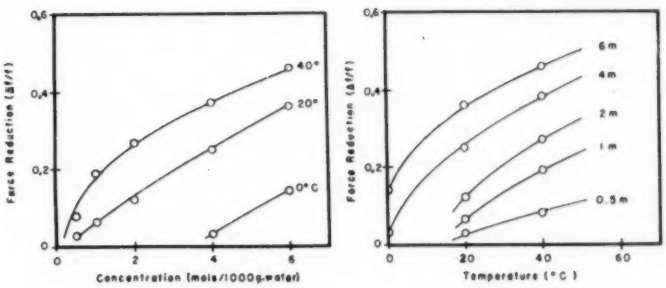

FIG. 3. *Instantaneous effect of nitric acid on water-saturated seed cotton.*

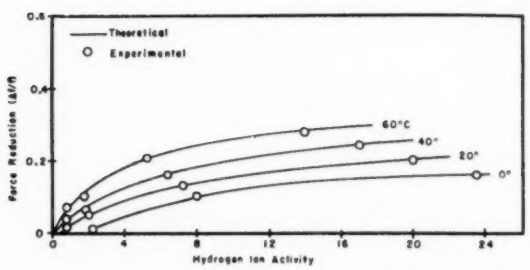

FIG. 4. *Instantaneous effect of hydrochloric acid on water-saturated seed cotton.*

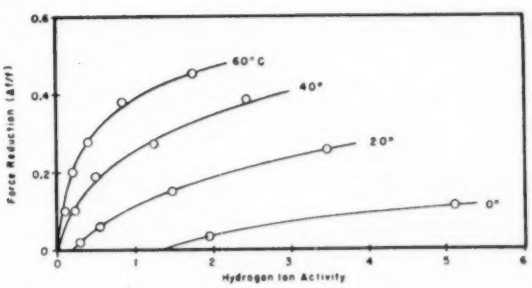

FIG. 5. *Instantaneous effect of sulfuric acid on water-saturated seed cotton.*

of hydrochloric and sulfuric acids with water-saturated seed cotton fibers are given in Table IV.

This reaction was treated as a pseudo-equilibrium because it is not a true equilibrium in that it is not reversible. However, it has many of the properties of an equilibrium. It was observed that when a fiber was treated successively with increasingly concentrated acid solutions, the total force reduction at each stage was the same as that obtained when the fiber was treated with the most concentrated solution alone. For example, the fiber was treated with 1 molal sulfuric acid (20°C), and a force reduction of 2% occurred; this solution was removed and 2 molal sulfuric acid added, with an additional force reduction of 4% occurring. The total force reduction, 6%, was the same as that obtained when

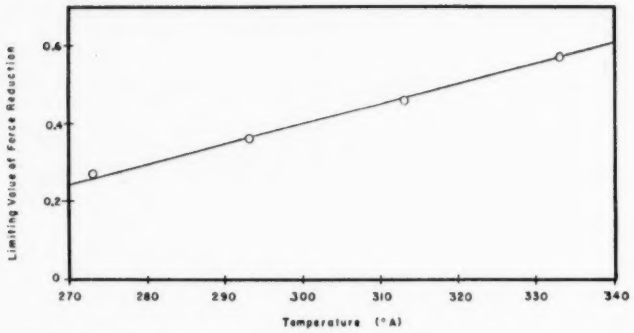

FIG. 6. *Variation of the limiting value of the force reduction with temperature*

a fiber was treated with 2 molal sulfuric acid. When the fiber was treated with these solutions in the reverse order, only the more concentrated solution caused any force reduction.

The limiting value of the force reduction, within experimental error, was the same for sulfuric and hydrochloric acids. This limiting value of the force reduction varies in a regular manner with the temperature, as shown in Figure 6. It is thought that this limiting value is a function of the accessibility of the fiber, and, if this is the case, the accessibility varies with the temperature.

The interchain structure is considered as one of the important factors for governing the properties of a fiber [8, 13]. It is generally believed that cotton fibers have regions of high order and regions of random arrangement. There is probably a gradual transition between the two regions [2], and there is evidence to show that dilute acid solutions do not penetrate the crystalline region [11]. There have been numerous attempts to determine the accessibility of cellulosic fibers [1, 2, 4, 5, 10, 11, 12]; however, there is very little correlation between the various methods [4].

The correlation of the limiting value of the force reduction to the accessibility is a problem in fiber structure. Since the limiting value is well below 100% at ordinary temperatures, this precludes the possibility of a continuous disordered region throughout any cross-sectional area in the wet fiber, and requires the continuous phase to be the ordered region. If, as it is thought, the crystalline regions are partly converted into disordered regions with increasing temperature, there is the possibility that a small conversion might serve to connect a previously inaccessible disordered region to the accessible regions. The linear relationship of the limiting value of the force reduction (*lvfr*) and temperature indicates that this is not the case. The magnitude of *lvfr* is of the same order as would be expected, using x-ray technique to determine the quantity of the disordered regions; thus, with reservation as to the validity, the *lvfr*, given in Table V, was taken as a direct measure of the accessibility or of the amorphous fraction.

The variation with temperature suggests there is an equilibrium between the ordered and the disordered regions:

$$(\text{cellulose})_c \overset{K}{\rightleftharpoons} (\text{cellulose})_a; \qquad \text{(B)}$$

TABLE V. VARIATION OF THE LIMITING VALUE OF THE FORCE REDUCTION WITH TEMPERATURE

Temperature (°C)	*lvfr* (%)
0	27
20	36
40	46
60	57

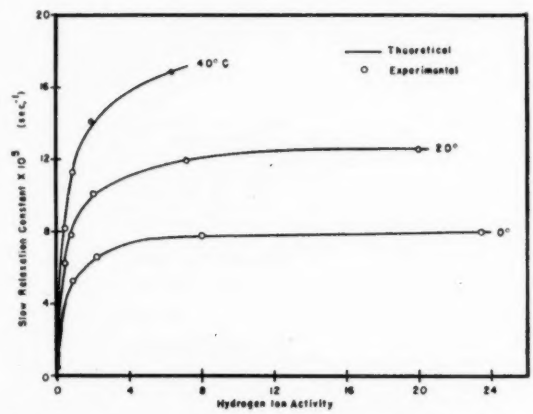

FIG. 7. *Effect of hydrochloric acid on slow relaxation constant of water-saturated seed cotton.*

and the equilibrium constant is given by

$$K = \frac{(\text{cellulose})_a}{(\text{cellulose})_c}. \quad (4)$$

Using the proposal relating *lvfr* to the accessibility, the equilibrium constant is given by

$$K = \frac{(lvfr)}{(100 - lvfr)}. \quad (5)$$

The equilibrium constant was evaluated at several temperatures, and the thermodynamic expression

$$\Delta F^\circ = -RT \ln K \quad (6)$$

was used to calculate the free energy of the conversion. The enthalpy of conversion of crystalline cellulose to amorphous cellulose was found to be 4 kcal., and entropy 12.4 e.u.

The acids had a more pronounced effect on the slow than on the fast relaxation constants. The effect of hydrochloric acid as a function of the hydrogen ion activity is shown in Figure 7, and that of sulfuric acid is shown in Figure 8. The effect of nitric acid on the basis of concentration is shown in Figure 9. A comparison of the effect of hydrochloric and sulfuric acids is shown in Figure 10, and for hydrochloric and nitric acids in Figure 11.

While it would have been desirable to have measurements at 60°C, it was impossible to collect measurements of sufficient accuracy due to the fibers rupturing shortly after the addition of the hydrochloric and sulfuric acid solutions, and almost immediately upon addition of the stronger nitric acid solutions. The slow relaxation constants with values greater than roughly 10^{-4} sec.$^{-1}$ have a degree of uncertainty due to the difficulty of obtaining a fiber that would withstand the experimental conditions for sufficient time for a very accurate evaluation of the relaxation constants.

The trend of the relaxation constants suggests that here again there is an equilibrium between the fiber and the acid solution. It was assumed that the first reaction was the adsorption of the acid (as the ions) and the second reaction between the acid and the fiber; thus the preliminary equilibrium is

$$\text{cellulose} + H^+ \overset{K}{\rightleftharpoons} \text{cellulose} - H^+. \quad (C)$$

The slow relaxation constant varies with the progress of the reaction to the right:

$$r_s = r_{s_0}\,(\text{cellulose}) + k'\,(\text{cellulose} - H^+). \quad (7)$$

The equilibrium for the adsorption of the hydrogen

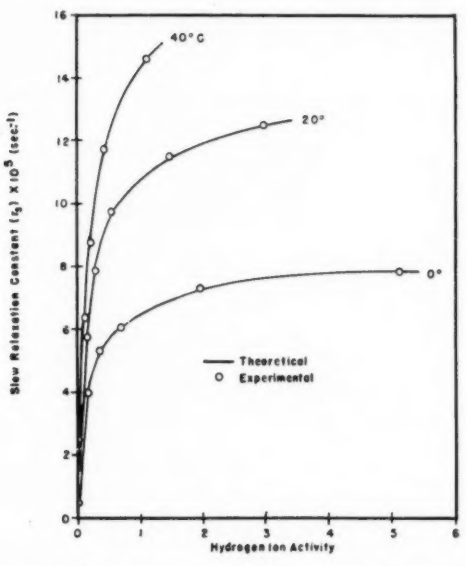

FIG. 8. *Effect of sulfuric acid on slow relaxation constant of water-saturated seed cotton.*

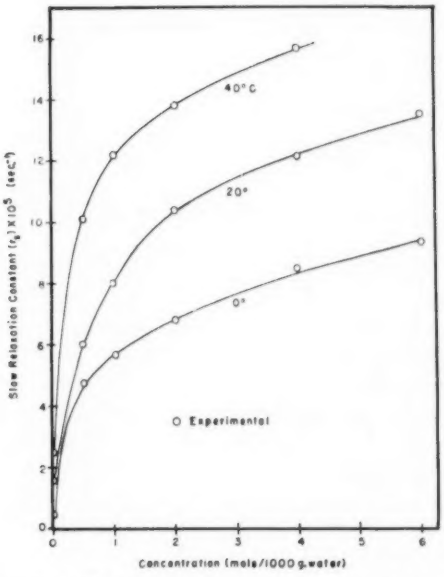

FIG. 9. *Effect of nitric acid on slow relaxation constant of water-saturated seed cotton.*

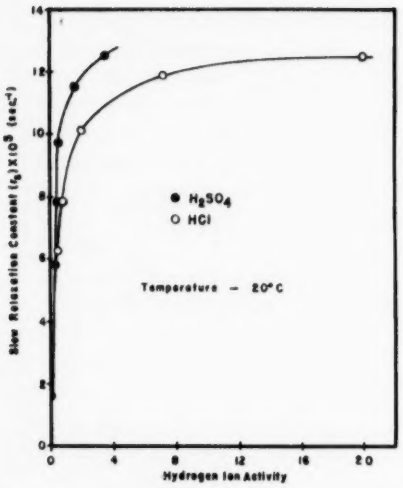

FIG. 10. *A comparison of the slow relaxation constant in hydrochloric and sulfuric acids.*

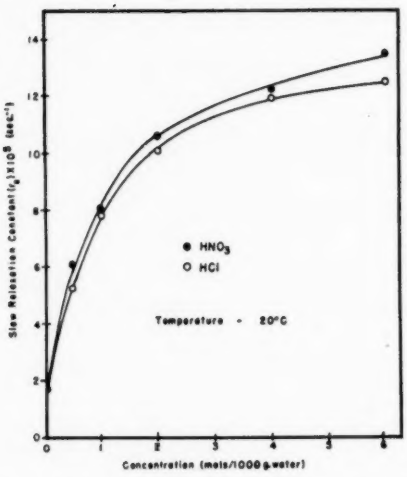

FIG. 11. *A comparison of the slow relaxation constant in hydrochloric and nitric acids.*

ion by the fiber is given by

$$K = \frac{(\text{cellulose} - \text{H}^+)}{(\text{cellulose})(\text{H}^+)} . \quad (8)$$

The total cellulose is the sum of the reacted and the unreacted cellulose:

$$(\text{cellulose})_o = (\text{cellulose}) + (\text{cellulose} - \text{H}^+) \quad (9)$$

$$(\text{cellulose})_o = (\text{cellulose}) + (\text{cellulose})K(\text{H}^+). \quad (10)$$

The amount of unreacted cellulose at any concentration is given by

$$(\text{cellulose}) = \frac{(\text{cellulose})_o}{1 + K(\text{H}^+)} . \quad (11)$$

Thus, the relaxation constant becomes

$$r_s = \frac{[r_{so} + k'K(\text{H}^+)]\,(\text{cellulose})_o}{1 + K(\text{H}^+)} . \quad (12)$$

The mol fraction, $(\text{cellulose})_o$, must have a value of unity; and thus the variation of the relaxation constants with hydrogen ion activity. The values obtained for the equilibrium constants and the rate constants for hydrochloric acid are given in Table VI, and those for sulfuric acid in Table VII.

The interesting observation at this point is the fact that the reaction constants for the sulfuric and hydrochloric acids are essentially the same. This indicates that the action of the acids is the same, and the difference in the behavior of the acids lies in the adsorption reaction. The reaction constants are thought to be related to the hydrolysis constants of the *beta*-glucosidic linkages.

The hydrolysis of the *beta*-glucosidic linkages is a complex process when the nature of the fragments are considered; however, a number of authors, including Nelson and Conrad [9], Ziifle *et al.* [11], Ekenstam [3], and others, have treated the over-all reaction as a first-order reaction with good results. Although the rate constants obtained in these studies obey the classical laws of kinetics, this treatment is not entirely satisfactory since the rate constants vary

TABLE VI. EQUILIBRIUM CONSTANTS AND REACTION CONSTANTS FOR HYDROCHLORIC ACID ON WATER-SATURATED SEED COTTON FIBERS

Temperature (°C)	K	k' (sec.$^{-1}$)
0	2.07	8.12×10^{-5}
20	1.51	12.9
40	1.41	18.4

TABLE VII. EQUILIBRIUM CONSTANTS AND REACTION CONSTANTS FOR SULFURIC ACID ON WATER-SATURATED SEED COTTON FIBERS

Temperature (°C)	K	k' (sec.$^{-1}$)
0	4.38	8.17×10^{-5}
20	4.08	13.3
40	3.06	18.3

TABLE VIII. APPARENT AND CALCULATED HYDROLYSIS RATE CONSTANTS FOR CELLULOSE

Temperature (°C)	Acid	Concentration	k'_e (sec.$^{-1}$)	k'_h (sec.$^{-1}$)	Literature source
0.12	sulfuric	65%	2.4×10^{-7}	1.8×10^{-5}	[3]
18	hydrochloric	5*N*	5.5×10^{-6}	1.5×10^{-5}	[8]
18	sulfuric	51%	1.8×10^{-6}	1.5×10^{-5}	[8]
20	sulfuric	65%	7×10^{-6}	25×10^{-5}	[3]
23	hydrochloric	fuming	6×10^{-5}	160×10^{-5}	[15]
30	sulfuric	51%	1.2×10^{-6}	7.1×10^{-5}	[8]

with the hydrogen ion activity. The data from these studies indicate that the first-order reaction approach is basically correct, but that all factors have not been considered.

Using the development previously cited, reaction (C), for the reaction of cellulose with hydrogen ions, the rate of hydrolysis is given by:

$$-d\,(\text{cellulose})/dt = k'_h\,(\text{cellulose}\cdot\text{H}^+) \qquad (13)$$

$$-d\,(\text{cellulose})/dt = k'_h K(\text{H}^+)\,(\text{cellulose}) \qquad (14)$$

$$-d\,(\text{cellulose})/dt = \frac{k'_h K(\text{H}^+)\,(\text{cellulose})_o}{1 + K(\text{H}^+)}. \qquad (15)$$

When this is compared with the usual expression for the hydrolysis:

$$-d\,(\text{cellulose})/dt = k'_a\,(\text{cellulose}), \qquad (16)$$

it is seen that the actual hydrolysis constant (k'_h) is related to the experimentally measured rate constant (k'_e) by the expression

$$k'_h = \frac{k'_e[1 + K(\text{H}^+)]}{K}. \qquad (17)$$

TABLE IX. EQUILIBRIUM AND REACTION CONSTANTS FOR HYDROCHLORIC ACID ON WATER-SATURATED SEED COTTON FIBERS

Temperature (°C)	K	k' (sec.$^{-1}$)
0	0.750	1.09×10^{-2}
20	0.425	1.25×10^{-2}
40	0.312	1.31×10^{-2}

TABLE X. EQUILIBRIUM AND REACTION CONSTANTS FOR SULFURIC ACID ON WATER-SATURATED SEED COTTON FIBERS

Temperature (°C)	K	k' (sec.$^{-1}$)
0	0.60	1.15×10^{-2}
20	1.33	1.27×10^{-2}
40	1.60	1.31×10^{-2}

Although the hydrogen ion appears in the expression for the hydrolysis of the cellulose (equation (15)), this factor is generally not included in the rate expression since the reaction is normally carried out in excess acid solution.

Taking the equilibrium constants from the slow relaxation constant treatment, the rate constant for the hydrolysis constant was calculated from some of the apparent rate constants found in the literature in the range of the present relaxation studies. Table VIII lists the apparent and calculated rate constants at various temperatures.

From the values obtained in Table VIII, it appears that the proposed treatment leads to fairly consistent results in the low concentration range and that a major divergence occurs at high concentrations of the acids. The activity of the acids is much greater than unity, and it is possible that at high activity the adsorption of the hydrogen ion is relatively unimportant.

It is noted that the hydrolysis constants for the cellulose in the low concentration range are somewhat smaller than the constants identified in the slow relaxation treatment as those for the hydrolysis reaction. This is as expected, since it is well known that a force alters the potential barrier. The force may alter the equilibrium constant for the adsorption of the hydrogen ion, but it is probable that such an effect would be small.

The acid has only a slight effect on the fast relaxation constant. In view of the previous treatment of the slow relaxation constant, it seemed reasonable to treat the fast relaxation process in a similar manner. However, the hydrogen ion is thought to react with another constituent, *A*, other than cellulose in the cotton fiber. The exact substance the hydrogen ion reacts with is not evident, but it is thought that it may be easily hydrolyzable material [15]. Thus, the reaction is written:

$$A + \text{H}^+ \underset{}{\overset{K'}{\rightleftharpoons}} A\cdot\text{H}^+. \qquad (D)$$

The development was analogous to the reaction with cellulose, and this gave the expression for the relaxation constant:

$$r_f = \frac{[r_{fo} + k'K(H^+)]A_o}{1 + K(H^+)} . \qquad (18)$$

As for cellulose, the activity of A_o was taken as unity, and the various constants were evaluated. These constants for the hydrochloric acid are given in Table IX, and for sulfuric acid in Table X.

As in the case of the effect of the acids on cellulose, the rate constant is independent of the acid and the difference in the acid occurs in the adsorption of the acid. The results of Ziifle *et al.* [11] indicate the possibility of this type of reaction. In their work apparently there was an extremely rapid hydrolysis of the fiber during the first hour of reaction, with slower hydrolysis of the accessible portion of the fiber occurring during the next 5 to 10 hrs. The oxidation studies by Harris *et al.* [14] show the presence of a very reactive component in the raw fiber, but it was identified as the pectin.

Thus, it is proposed that the relaxation element participating in the fast relaxation process is easily hydrolyzable material.

Although a quantitative treatment of the nitric acid data was not possible due to the lack of good activity data, it is apparent that the effect of the nitric acid is substantially the same as observed for hydrochloric and sulfuric acids. In the temperature range of the experiments, the oxidizing power of nitric acid does not appear to be an important factor. However, the results of the work at 60°C indicate that the oxidizing power becomes an important aspect of the reaction.

The surprising regularity of the various effects of hydrochloric and sulfuric acids gives a very strong indication that the important factor in the reaction of these acids with the fiber is the extent of adsorption of the acid by the fiber, and that the secondary reaction of the hydrogen ion with the fiber is essentially the same. The obvious question arises from this work as to whether or not the adsorption of the acid by the fiber is the important step in the reaction of all acids with cotton fibers. Further experimental evidence is needed to settle this point.

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Impact Properties of Yarns Made from Different Fibers

Herbert F. Schiefer, Wm. D. Appel, John F. Krasny,* and George G. Richey

Textiles Section, National Bureau of Standards, Washington, D. C.

Abstract

Yarns ranging from low tenacity and high elongation to high tenacity and low elongation were broken by impact loading and by static loading. The energy required to break each yarn under impact loading, "impact energy," and under static loading, "static energy"; the elongation at break; and the tenacity were measured or calculated.

The results show that the impact energy to rupture can, in general, be estimated from the static energy. The impact energy greatly exceeded the static value for yarns of low elongation. For yarns breaking above an elongation of about 50%, the impact energy was about equal to the static energy, except for two yarns having an elongation of over 500%, where it was less than the static value.

Yarns having a very high elongation when tested at 70°F and 65% relative humidity had greatly reduced elongation when dried for 120 hrs. at 190°F and tested immediately. The elongation was still further reduced when the dried yarns were cooled for 1 hr. at −40°F and tested immediately.

These findings have a bearing on the selection of yarns for the construction of safety belts, safety ropes, and certain aeronautical textiles which may be subjected to impact loading over a wide range of temperatures.

Introduction

The properties of textiles under impact loading are of increasing importance to agencies concerned with national defense. They are also of great interest to safety engineers and manufacturers of safety belts and ropes for civilian use, where the lives of individuals may depend upon the capacity of the material to absorb the energy of impact. Published information is not only meager, but also appears to be contradictory. Newman and Wheeler [2] published results on the impact strength of nylon and sisal ropes which indicate that energy values computed from static tests of these ropes give a good estimate of the performance under impact loading. Stang, Greenspan, and Newman [4] published results on dynamic tensile tests of cotton and nylon webbing. Whereas the cotton webbing showed higher capacity for energy absorption when tested under impact loading than when tested under static loading, the reverse was found for nylon webbing. Kaswell [1] showed that the static energy and elongation may vary greatly with temperature. Wegener and Geuthe [5] recently reported results for various yarns, with elongations less than 40%, which indicate that the stress and extension for impact loading are consistently less than for static loading. Accordingly, the energy absorption for impact loading would be considerably less than for static loading.

In view of the importance of the capacity of textiles to absorb energy and of the interest in such information for materials of very high elongation, an exploratory study was made on yarns ranging from very high elongation and low tenacity to low elongation and very high tenacity. The results of this study are reported and discussed in the present paper.

Materials

The 21 yarns tested included a wide range of materials, many of them still in the experimental stage of development at the time the work was done, and a wide range of constructions. They are listed in Table I.

Testing Procedures

General

Unless otherwise stated, all tests were made on specimens of yarn which were in equilibrium with an atmosphere maintained at 70° ± 2°F and 65 ± 2% relative humidity.

* Present address: Harris Research Laboratories, Washington, D. C.

TABLE I. MATERIALS

Sample No.	Description	Filaments	Denier	Twist
1	Polyethylene, undrawn	1	3820	none
2	Nylon, undrawn, treated	34	2165	1Z
3	Nylon, undrawn	17	1185	1Z
4	Nylon, undrawn, treated	34	1163	1Z
5	Nylon, undrawn, treated	34	1195	1Z
6	Acetate, high impact	52	343	3S
7	Vinyl chloride-acrylonitrile copolymer, 70% elongation	200	407	12Z
8	Vinyl chloride-acrylonitrile copolymer, 50% elongation	200	329	4Z
9	Vinyl chloride-acrylonitrile copolymer, 40% elongation	200	305	4Z
10	Vinylidene chloride-vinyl chloride copolymer	1	840	none
11	Vinylidene chloride-vinyl chloride copolymer	1	1235	none
12	Vinylidene chloride-vinyl chloride copolymer	16	220	6Z
13	Rayon, viscose	480	1135	3Z
14	Acrylonitrile, 3-strand sewing thread	1	945	20S(10Z)*
15	Nylon, 3-strand sewing thread	1	1060	0(10Z)*
16	Nylon	1	318	none
17	Silk	—	788	12S(9Z)*
18	Nylon	17	258	1Z
19	Rayon, viscose, high strength, 3-strand sewing thread	—	917	14S(12Z)*
20	Polyester	34	206	2.5Z
21	Nylon	34	208	1Z

* Figures in parentheses give cord twist.

For the breaking strength and impact tests, the ends of each yarn specimen were glued to tabs of cardboard with suitable adhesives before they were fastened in the clamps in order to minimize slippage and damage of the yarns in the clamps. The ends of the yarn specimens nos. 1, 2, 3, 4, and 5 were drawn before they were glued to the cardboard tabs to assure a satisfactory bond.

Breaking Strength, Static

The breaking strength tests were made with the Tinius Olsen electromatic testing machine with a

TABLE II. RESULTS OF TESTS

Sample No.	Tenacity (g./den.)	Elongation (%)	Static energy (in.-lb./in. den.)	Impact energy (in.-lb./in. den.)	Impact energy / Static energy (%)	Recovered energy* (%)
1	0.3	750	26 $\times 10^{-4}$	27.5 $\times 10^{-4}$	106	3
2	0.6	550	41	37.0	90	5
3	0.7	570	65	49.5	76	8
4	0.8	420	57	74	130	9
5	1.1	420	58	61	105	7
6	1.1	37	6.5	10.7	165	6
7	1.7	66	16.2	18.0	111	9
8	2.0	45	11.5	15.5	135	12
9	2.3	38	10.9	14.7	135	13
10	1.9	26	6.7	7.5	112	46
11	2.0	24	5.6	6.8	121	40
12	2.0	13	2.5	5.6	224	73
13	3.0	9	3.8	6.8	179	32
14	3.0	17	6.1	14.5	238	28
15	3.5	20	6.9	12.5	181	75
16	3.9	13	4.9	15.5	316	67
17	5.2	15	10.9	15.0	138	33
18	5.9	14	8.2	10.3	126	59
19	6.0	8	5.0	9.8	196	37
20	6.6	12	10.2	15.3	150	60
21	6.7	16	13.4	16.5	123	63

* Energy recovered is expressed as a percentage of the energy input at 80% of the breaking strength.

distance of 10 in. between grips, except in testing yarns nos. 1, 2, 3, 4, and 5, where this distance was 2 in., and with a rate of elongation of 12 in./min. Tests made at this rate of elongation may be considered static tests. The load-elongation curves were automatically recorded on rectilinear coordinate paper. At least five specimens of each yarn were tested. The average breaking strength, converted to tenacity in grams per denier, and the average percentage elongation at rupture were computed from the graphs. The results are given in Table II.

The area under the load-elongation curve of each specimen was measured with a planimeter. The average area for at least five specimens was computed. It is a measure of the static energy required to strain the yarn to rupture. The static energy, expressed in inch-pounds per inch of length of yarn and per denier, is given in Table II.

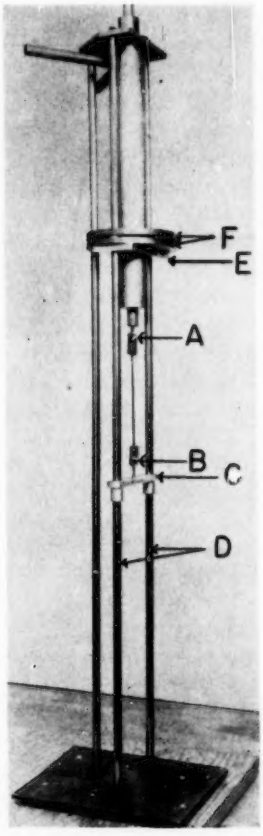

FIG. 1. *Improvised equipment for impact tests.*

Impact Strength

The equipment shown in Figures 1 and 2 was improvised for estimating the impact strength of the yarns. The cardboard tab on one end of a specimen is attached to the fixed hook *A*, and that on the other end to hook *B* of a light aluminum plate, *C*. The distance between the tabs was 10 in., except for yarns nos. 1, 2, 3, 4, and 5, where it was 2 in. The plate *C* is free to move vertically along the two parallel rods, *D*. A second aluminum plate, *E*, weighing ¼ lb., is also free to move along the rods. It serves as the impact load. It can be raised to a known distance above plate *C*, and allowed to drop on it under essentially free fall. The distance of the free fall can be varied up to 20 in. Weights, *F*, in increments of ¼

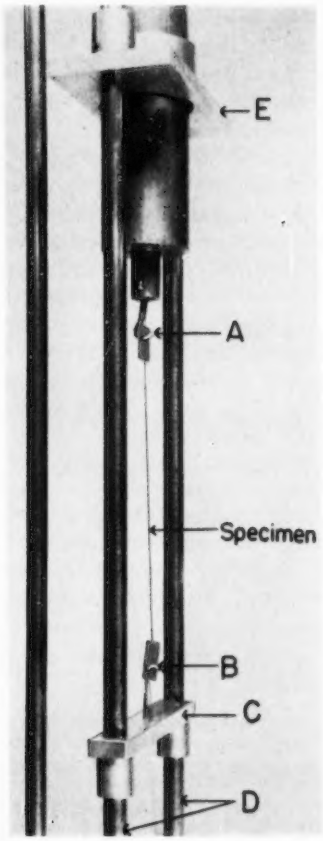

FIG. 2. *Close-up view of specimen mounted in the equipment for an impact test.* A—*Fixed hook.* B—*Movable hook.* C—*Movable aluminum plate.* D—*Parallel rods guiding plate* C. E—*Aluminum impact plate.* F—*Impact weight.*

lb., can be added to plate E as required for the tests. The rate of elongation at impact was of the order of 6,000 in./min., or about 500 times that in the static tests.*

Five specimens of each yarn were tested, using a total weight and height of fall such that the energy at impact was insufficient to break any of the five specimens of a given yarn. The energy at impact was then increased in equal increments and at least five specimens were tested for each impact energy. The number of specimens which failed at each impact energy was recorded. The energy at impact was increased until all five specimens of a yarn tested failed for that energy. The extensions of the unbroken specimens for those energies at impact where only some of the five specimens failed were measured after the impact weight had come to rest. The average of these values is an approximation of the extension at rupture. The impact energy to rupture of the broken specimens was taken to be equal to the energy at impact plus the product of this extension and the total weight of the impact mass.†

The percentage of specimens which failed at a given impact energy, expressed in inch-pounds per inch of length of yarn and per denier, was plotted against the impact energy. A straight line could be fitted to the plotted points. The average impact energy to rupture of a number of specimens of a yarn is therefore given by the point on the straight line at which 50% of the specimens failed. These values are given as the impact energy in Table II.

Energy of Recovery

Some of the yarns were loaded statically in the Tinius Olsen electromatic testing machine to 80% of the average breaking strength and then the load was removed. From the area under the load-elongation curve the energy input was computed. From the area under the load-recovery curve the energy recovered was computed. The energy recovered, expressed as a percentage of the energy input, is given in Table II.

Elongation of Oven-Dried Specimens

Specimens of some yarns were dried for 120 hrs. in an oven maintained at 190°F. As each specimen was removed from the oven it was immediately extended to rupture with the hands, and the elongation to rupture was observed qualitatively.

Elongation of Oven-Dried Specimens at Low Temperature

Specimens which were dried for 120 hrs. in an oven maintained at 190°F, and were therefore essentially dry, were immediately transferred from the oven to a desiccator which was placed for 1 hr. in a conditioning box maintained at −40°F. As each specimen was removed from the desiccator in the cold conditioning box it was immediately extended to rupture with the hands, and the elongation to rupture was observed qualitatively.

Discussion of Results

Although the yarns varied in number of filaments, denier, and twist, the results nevertheless reflect basic differences. Thus the energies, both static and impact, to break the yarns of low tenacity and very high elongation were relatively high. The recovered energies for the yarns of high and very high tenacity and ordinary elongation ranged from moderately high to very high. These values are pertinent in the choice of shock-absorbing fibers for use in safety appliances.

The impact energies to rupture of the yarns of very high elongation, nos. 1, 2, 3, 4, and 5, are about equal to their corresponding static energies. On the other hand, the yarns having high or very high tenacity and ordinary elongation, nos. 12, 13, 14, 15, 16, 17, 19, and 20, have values for impact energy to rupture which are considerably greater than the static energies.

The impact energy to rupture is plotted against the static energy in Figure 3. At low impact energy, the values exceed the static energy: all of the points

* It is important to note that whereas the rate of elongation in the static tests remained constant at 12 in./min. throughout the test, in the impact tests the rate of elongation decreased from about 6,000 in./min. at impact to zero at rupture. Obviously quite different results would be expected for impact tests where the high rate of elongation is maintained throughout the test. Although tests of the latter would provide basic information concerning the properties of the materials tested, the impact tests described in this paper provide important information concerning those practical applications, such as in the use of safety ropes and belts or protective armor, where it is essential that the rate of elongation becomes zero before the material is ruptured.

† This total impact energy is a close approximation to the impact energy at rupture. The energy recovered in static tests when yarns of high elongation were loaded to 80% of the breaking strength was less than 10% (Table II) so that the error in the total impact energy would be less than 5% even if the product of yarn extension and impact weight were as large as the energy at impact. The energy recovered in static tests when yarns of low elongation were loaded to 80% of the breaking strength was less than 75% (Table II) so that the error in the total impact energy would again be small because for these yarns the product of yarn extension and the impact weight is less than 20% of the energy at impact.

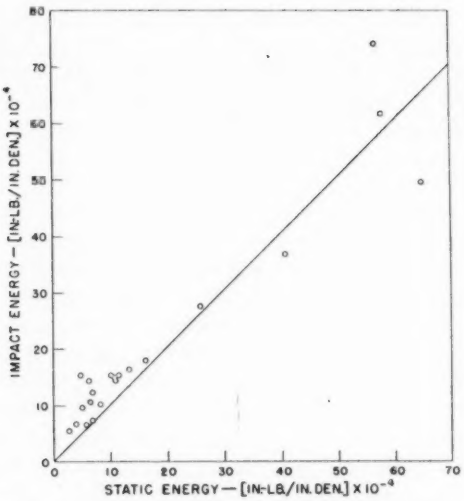

FIG. 3. *The impact energy of the yarns plotted against the static energy.*

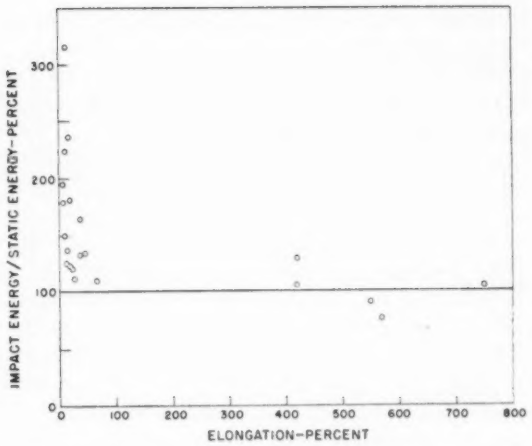

FIG. 4. *Impact energy to rupture of the yarns, expressed as a percentage of static energy, plotted against the elongation.*

lie above the 45° line. At high impact energy, the values are about equal to the static energy: the points lie slightly above and below the 45° line. Thus, static energies give, in general, a good estimate of the impact energies to strain the yarns to rupture.

The impact energy to rupture, expressed as a percentage of the static energy of each yarn, is plotted against the elongation in Figure 4. Many of the plotted points below an elongation of 50% lie considerably above 100%, indicating that the impact energy to rupture is much greater than the static energy.* For elongations above 50%, the impact energy to rupture is about equal to the static energy; the points lie close to the line drawn through 100%.

The relationship between the tenacity and elongation is shown in Figure 5. The yarns having elongations below 50% vary in tenacity from 1 to 7 g./den. The yarns having tenacities below 2 g./den. vary in elongation from 26% to 750%.

There appears to be no general relationship between the tenacity and impact energy to rupture of the yarns, or between the impact energy to rupture and elongation. Evidently neither the tenacity nor the elongation alone can be used for estimating the impact energy to rupture.

The values of energy recovered, expressed as a percentage of the energy input when the yarn is loaded to 80% of the breaking strength, give an indication of the portion of the total energy stored in the yarn. Safety equipment made from yarn that has the ability to store a large portion of the total energy developed in stopping the fall of a man will jerk him upward. This would increase the hazard to the man.

A low value for energy recovered, as for yarns nos. 1, 2, 3, 4, 5, 6, 7, 8, and 9, indicates that there will be little or no rebound. It also indicates that the material will be permanently stretched and therefore no longer effective for absorbing an impact load. Safety equipment made from such material would be unsuitable for further use after an impact load that utilizes any considerable part of its energy-absorbing ability. The increased length and change in appearance of the

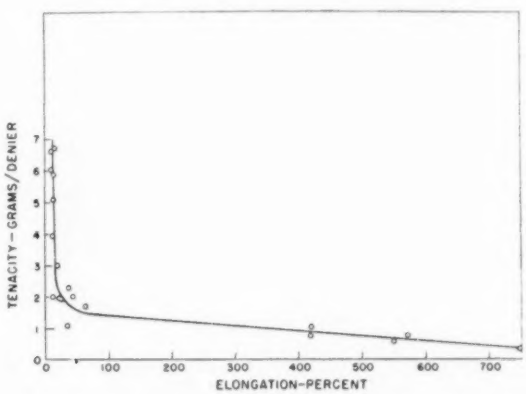

FIG. 5. *Relationship between tenacity and elongation.*

* The results of Wegener and Geuthe [5] show the reverse effect. Unfortunately it is impossible to examine their results critically for a possible explanation of this reversal because insufficient details are given for the impact testing conditions.

elongated member should be a clear indication of the loss of value and necessity for replacement.

The results also indicate that yarns nos. 1, 2, 3, 4, and 5 exert less force at the clamped ends for a given impact energy absorption than any of the other yarns tested. This is an important factor to consider in relation to the strength of the anchor and also the decelerating force that the human body can withstand.

Yarns nos. 1, 2, 3, 4, and 5 showed a great reduction in elongation after drying for 120 hrs. in an oven at 190°F. A still greater reduction was found after cooling the dried specimens in a desiccator for 1 hr. at a temperature of − 40°F. Yarns nos. 7, 18, 20, and 21, when similarly tested, showed essentially no change in elongation. Under these conditions the impact energies to rupture of the first group would be greatly reduced, with no appreciable change for the second group. The dried specimens of the first group quickly recovered the high elongation after they were allowed to regain moisture from the atmosphere of the room. These qualitatively observed changes in the elongation of the yarns are in substantial agreement with the results of quantitative static tests made by Kaswell [1] at 70°F and at − 70°F. At − 70°F the tenacity of undrawn nylon was increased from 1.0 to 1.2 g./den., whereas the elongation was decreased from 373% to 16%. The static energy to rupture was decreased from 46.6×10^{-4} to 3.5×10^{-4} in.-lb./(in. den.). At − 70°F the tenacity of fully drawn nylon was increased from 8.0 to 9.3 g./den., the elongation was increased from 12.3% to 12.7%, and the static energy to rupture was increased from 10.3×10^{-4} to 12.0×10^{-4} in.-lb./(in. den.).

It should be pointed out that the true value of a property obtained in a test on a yarn is not realized when the yarn is used to make a complex structure, such as a rope. For some materials, the value of a property, such as breaking length or tenacity, in a complex structure such as a rope may be only 25% of the value obtained for the yarn [3]. This fact and also the possible change in a property under high or low temperature and extremely low relative humidity must be given serious consideration in the selection of a material for safety ropes and safety equipment.

Since the values of the mechanical properties of yarns are, in general, not realized when they are made into a complex structure, such as a rope or webbing, the data given for the yarns in this paper cannot be used directly to predict the properties of a rope or webbing made from them.

Excessive shock loads on the falling man and the anchor may develop when safety ropes made from yarns of very high tenacity and low extension are used. The same results would be obtained if an oversized rope of the low-tenacity and undrawn material were used since little or no drawing of the material would occur.

The results presented point to the need for impact tests of rope and webbing made from fibers currently used and from the new fibers that have high static energies and appear to be stable in their mechanical properties over the range of temperature and moisture conditions experienced by safety equipment. Safety equipment made from the rope and webbing should be similarly tested. This is important because in such equipment points of suspension may deviate critically in their behavior from the rest of the rope. For example, Stang *et al.* [4] found that nylon webbing broke under impact at the *D*-ring which formed its upper terminal and that the broken ends were fused, indicating insufficient dissipation of the heat created by the impact load at this point. The impact energy absorbed by the nylon webbing was less than the static energy. The relationship of load to elongation should be evaluated during the application of the impact load, and the effects of temperature, moisture conditions, and storage on the results should be ascertained. Such tests would determine the value of the newer materials for use in safety equipment and would provide information needed for the development of standardized performance tests for the materials and equipment.

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Investigation of the Frictional Properties of Textile Fibers under Variable Fiber Stress*

Bruce Gardner Hood†

INVESTIGATORS have given a discouraging outlook to the problem of determining the frictional characteristics of yarns and fabrics by pointing out the complex interrelationship that exists between the properties of the fiber, the yarn, and the fabric. One field of study has involved the frictional nature of the individual fibers and how it affects the processing characteristics and properties of the various textile structures which they comprise. Since such structures are in reality only geometrical complexities of the basic fiber, it is evident that the solution to the problem can best be achieved by a study of the frictional nature of the individual fibers. There is a definite need for an easy means of measuring this fiber property. A complete understanding of the frictional properties of the fibers would be of utmost value to the textile industry.

It was with this in mind that a study was undertaken by the author to develop a means of measuring the relative frictional properties of individual textile fibers.

Development of Apparatus

In the development of a fiber frictional testing device, it was thought essential that realistic consideration be given to the nature of fiber-to-fiber contact in textile materials. Thus, a machine embodying the principle of the fiber twist method was essential, because this most nearly approaches actual fiber-fiber contact conditions in textile materials. The method developed consists of suspending the fibers to be measured from the alternating arms of the machine under any desired tension by applying weights to the ends of the fibers. By inserting twist, the fibers are brought into contact; they are rubbed together vertically by the arms, which move alternately up and down 180° out of phase. The turns of twist are then increased until slippage of the fibers ceases. The number of turns of twist necessary to stop fiber slippage can be taken as an arbitrary unit of measure of the frictional resistance of the fibers being twisted.

The fiber frictional measuring device is shown in Figure 1. Figures 2 and 3 illustrate schematically the principle of its operation. Fibers *a* and *b* are each suspended by one end to the alternating arms *c* and *d*. Weights W'_a and W'_b are applied to the other ends of

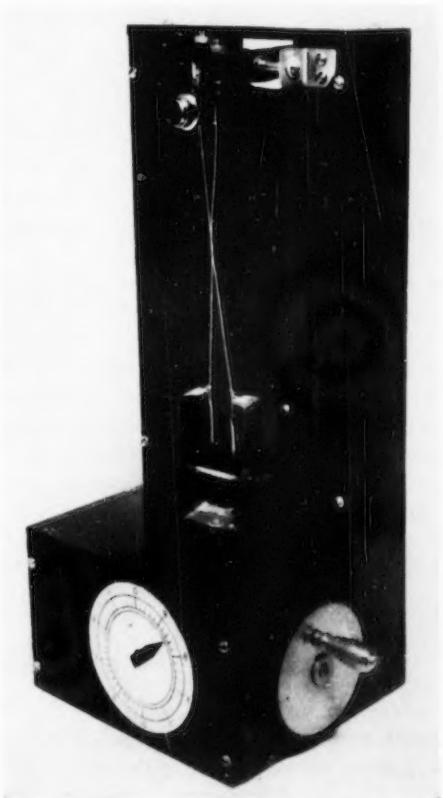

FIG. 1

* Presented in part at the Cotton Research Clinic, National Cotton Council of America, Pinehurst, N. C., Feb. 14, 1952.

This paper is based on a thesis for a B.S. degree in Business and Engineering Administration, Massachusetts Institute of Technology, June 8, 1951.

† U.S.A.F. Research and Development Command, Wright-Patterson Air Force Base, Dayton, Ohio.

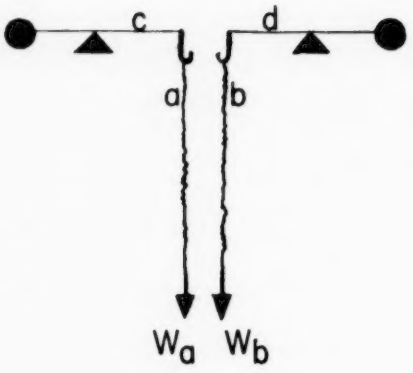

FIG. 2

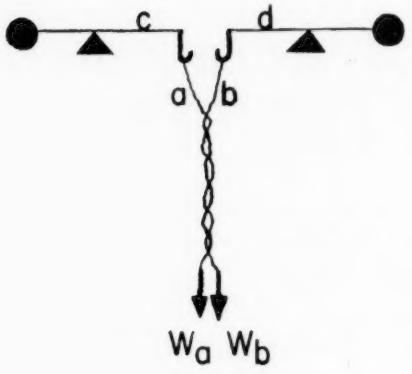

FIG. 3

the fibers. Figure 3 shows the fibers twisted together to produce the frictional drag against each other as the arms c and d are alternately raised and lowered.

The method is based on the theory for the measurement of friction between single fibers by the fiber twist method as developed by Lindberg and Gralén [3]. Figure 4 represents undistorted fiber twist, with the forces acting under low interfiber friction. Figure 5 shows distorted fiber twist, with the position of fibers and forces acting when interfiber friction causes fiber slippage to cease. β is the angle between two fibers in the twist; the area of contact is along the straight line A-A_1.

Consider two cylindrical fibers of the same diameter twisted about each other. Let P = applied tension to fibers, n = number of turns in the twist, μ = frictional coefficient, β = angle between the two fibers in the twist, N_t = total normal force between the two fibers, and N = normal force per turn.

Then, in accordance with the theory as given by Lindberg and Gralén, the normal force per turn can be expressed as

$$N = 2P\pi \sin \frac{\beta}{2}, \tag{1}$$

and the total normal force acting between the fibers at any value of n as

$$N_t = nN. \tag{2}$$

By assuming that the frictional coefficient is independent of the normal force and the area of contact, and that the applied tension is equal to the friction force when slippage stops, the applied tension can be expressed as

$$P = \mu N_t \tag{3}$$

or, from equation (2),

$$P = \mu N n. \tag{4}$$

By substituting the expression for N from equation (1) into equation (4),

$$P = \mu 2P\pi n \sin \frac{\beta}{2}. \tag{5}$$

By eliminating P and solving for μ,

$$\mu = \frac{1}{n2\pi \sin \frac{\beta}{2}}, \tag{6}$$

FIG. 4

FIG. 5

where $2\pi \sin (\beta/2)$ may be considered a constant for any setting of the device.

Thus, it can be seen that the coefficient of friction varies inversely with the number of turns, and an increase or decrease in n will indicate an inversely proportional increase or decrease in the coefficient of friction. The principle of the frictional testing device is basically contained in, and can best be explained by, equation (4). By referring to equation (4), it can be seen that the two fibers slipping by each other in contact will continue to slip until the number of turns of twist is increased to the point where the product of the terms on the right side of the equation, which is the frictional force between the fibers, is equal to the tension in the fiber, P, on the left side of the equation, which is the force causing the fibers to slip. Furthermore, by referring to equation (1), it can be seen that any change in the value of P will cause a proportional change in the value of N, and , therefore, as indicated in equation (6), n is dependent only on the coefficient of friction.

The present study is not concerned with the determination of absolute values of the frictional coefficients. The main objective is to show the relative frictional resistance offered by various textile fibers under various normal and tangential stresses. Calculation of absolute values of the frictional coefficients would be possible by using the relationships given by the theory presented for the fiber-twist method. The resulting relationships between the frictional coefficients and the normal pressure would be identical to the relationships found between $(1/n)$ and P since the coefficient affecting μ is directly proportional to $(1/n)$. The values of n obtained are, of course, subject to machine errors, but such machine errors cancel out when comparing fibers, and thus may be neglected for purposes of fiber comparison.

Preparation of Fibers for Testing

The problem is relatively simple for those natural fibers whose lengths are in excess of the distance between the suspension arms of the frictional testing device and the guide wires of the twisting mechanism, and also for continuous-filament synthetics which can be cut to the desired length. With such fibers and continuous filaments, it is only necessary to glue a small copper wire hook to each end of the fiber and then hang the fiber to one of the suspension hooks located on the arms of the device. The other end of the fiber is then passed through the corresponding guide wire on the twisting mechanism, with the hook on this end of the fiber being used for applying any desired stress to the fiber. The other fiber making up the pair is mounted in a similar manner from the other suspension hook and corresponding guide wire. For shorter natural fibers and staple synthetics the best method found is to glue a fine silk thread of the proper length to each end of the fiber. The other end of this silk thread is in turn glued to a small copper wire hook as before. Each fiber and thread assembly is then mounted in the device in the same fashion as with the longer fibers. It is essential that the fibers be positioned midway between the suspension hooks and the wire guides so that upon the insertion of twist fiber contact will first occur at the mid-point of each fiber. It is apparent that the minimum fiber length tested is limited by the length of the fiber twist necessary to stop slippage of the fibers.

The fibers tested were subjected to standard conditions (70°F and 65% relative humidity) for 4 hrs. prior to testing and during testing as far as facilities permitted.

It is essential that extreme care be taken to keep the fibers to be tested as clean as possible prior to testing. Thus, fibers should not be handled or placed where they are apt to pick up foreign matter that might contaminate the surface of the fiber.

Device Adjustments

After a pair of fibers to be tested is mounted in the device, it may be necessary to further align the fibers vertically and horizontally. Such adjustments can be made by the vertical adjustment screws on the arms and the helix adjusting screw, respectively.

The relative speed between the fibers, the length of travel of the fibers, and the helix angle between the fibers can all be varied by changing the frequency of oscillation of the arms through adjustment of the driving mechanism. The length of travel is varied by adjusting the length of travel of the arms. The helix angle can be varied by changing the distance between the arms and making a corresponding adjustment of the wire guides. For purposes of comparison of the various fibers tested, it was deemed essential that these variables remain constant throughout the tests. A frequency of oscillation of the arms of 10 c.p.m., a length of travel of $\frac{3}{4}$ in., and a helix angle of 6° were found to be the most satisfactory conditions for the tests.

Testing Procedure

After the fibers have been mounted and the necessary adjustments made, the fibers are brought just into contact and the indicator pointer is set at zero turns. The arms are now set in motion, and twist is inserted to the fibers until fiber slippage ceases. The number of turns required is observed and recorded, and the fibers are untwisted until the dial again reads zero turns. This procedure should be repeated until the values obtained are reasonably reproducible. The whole procedure should be repeated for values of applied fiber tension, P, ranging from 30 mg. to the point where fiber breakage occurs. Since a single fiber is required to carry the combined load carried by each fiber when fiber slippage ceases, the latter value is limited to one-half the tension strength of a single fiber. It is essential to take readings at various values of fiber tension in order to study the effect of crimp and fiber stress on the frictional coefficients. Only 2–5 pairs of fibers for each type of fiber were tested because it was decided that this was ample for the purposes of this investigation. By following the above procedure, the values of n obtained are for static friction. Kinetic friction values of n can be obtained by tapping the twisting device lightly, which will cause the fiber being held up by the static frictional force between the fibers to slip again. By repeating this process while increasing the turns of twist, a state is finally reached at which tapping will cause the previously held fiber to slip at an extremely low and constant velocity. This kinetic value of n is naturally dependent on the judgment of the observer, and, while it is easily observed with some types of fibers, it is hard to distinguish from the static value with other types of fibers.

It is important that the fibers be twisted very slowly (preferably one turn per cycle) so as to eliminate any build-up of torsional stress in the fibers due to twisting.

Results and Discussion

The friction-stress curves of the various textile fibers tested are shown in Figures 6–15. These graphs show the relationship between the reciprocal of the number of turns of twist, $1/n$, which is directly proportional to the coefficient of friction, μ, and the applied tension to the fiber, P, which increases in direct proportion to the normal force, N. The reciprocal of the number of turns of twist, $1/n$, was plotted as the ordinate so that the resulting curves would show a downward slope for a decrease in friction. Except as where specified to the contrary, all curves are for the static value of $1/n$.

It will be remembered that the theory is for an ideal case where two straight cylindrical fibers of the same diameter are twisted together, and where it is further assumed that the frictional coefficients are independent of the normal pressure and the area of contact. If these conditions and assumptions are considered to be valid for the fibers tested, then one would expect the relationship between $1/n$ and P to be a series of lines parallel to the P axis, with the distance of each line from this axis being dependent only upon the coefficient of friction of the pair of fibers being tested. Very few textile fibers approach this ideal case, and most investigators have shown that the coefficient of friction is dependent on the normal force and possibly on the area of contact. Inspection of the relationship between $1/n$ and P for the fibers tested shows that it is not of the form $n = \text{constant}$, but, rather, is described by a curve with a negative decreasing slope. The high values of $1/n$ at low values of P may be accounted for in the most part by the crimp present in most of the fibers at low values of P. They may also be due partly to the rigidity of the fiber at low values of P, causing a nonideal twist. This latter explanation may be more valid for the continuous-filament fibers where crimp is not present, but even in this case the fibers are frequently in a slightly wrinkled state while under low stresses. The calculations of/or coefficient of friction would be of little meaning and value in this range of the curves, but it is the frictional resistance found in this range of the curves that is of importance in sliver and rovings and therefore should be given ample consideration.

It was found essential that β be kept as small as possible when comparing various fibers. Thus, a value of approximately 6° for β was used.

The effect of a build-up of a static charge between the fibers during rubbing has been neglected since the tests were conducted at a relative humidity deemed sufficient to overcome such a build-up (although future investigation of fiber friction at a lower humidity may have to take the effect of static into account.

Cotton

Figure 6 gives an over-all picture of the relative frictional properties of the various cotton fibers tested. It should be observed that the long-staple fine American Upland has a higher clinging power than the short coarse Indian cotton. This is not in agreement with the results found by previous investigators that the coarser cottons have a higher clinging power. However, it will be noted that the Indian cotton does have a higher clinging power than the other finer cottons tested. Cotton fibers are usually crimped, but the crimp may be neglected at values of P greater than 200 mg. It should, however, be pointed out that the value of P at which the crimp is removed is extremely variable between different cottons as well as between fibers within the same variety. It is believed that the value at which the crimp is removed is an important property of the fiber with regard to its clinging power and one which deserves further study.

The clinging power of cotton is affected not only by the presence of crimp, but also by many other factors due to the complex nature of the fiber. A cotton fiber can best be described as a ribbon with

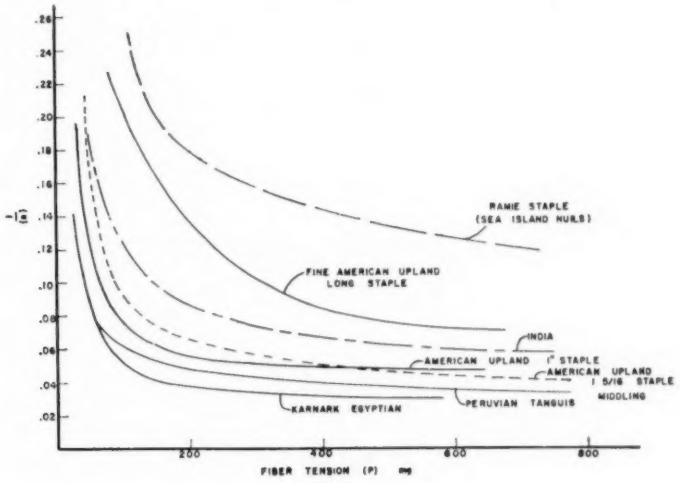

FIG. 6

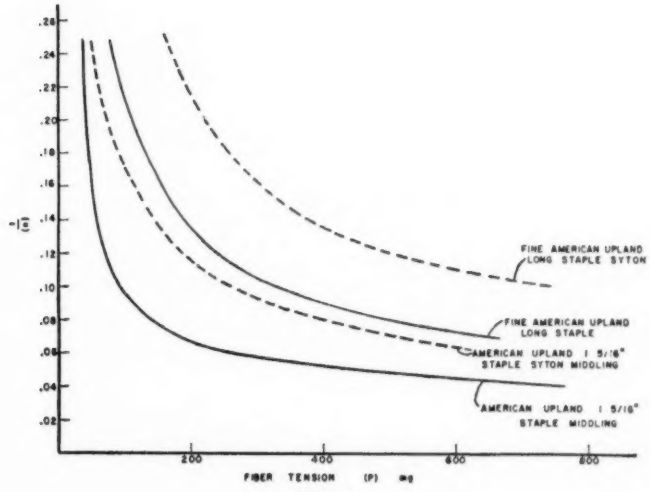

FIG. 7

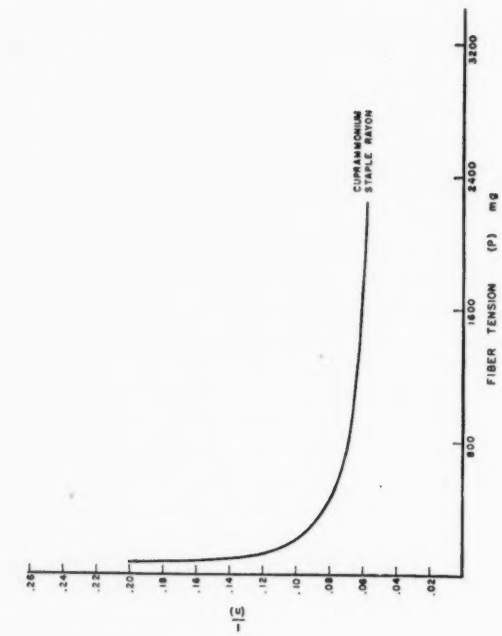

FIG. 9

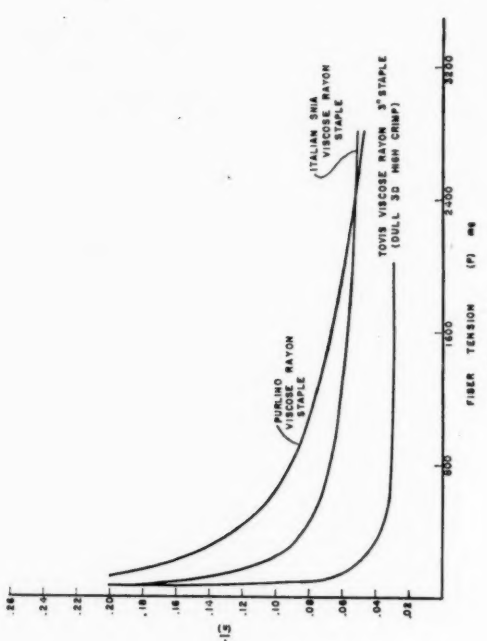
PURLINO VISCOSE RAYON STAPLE
(ITALIAN SNIA VISCOSE RAYON STAPLE
TOVIS VISCOSE RAYON 3" STAPLE (DULL 3D HIGH CRIMP)
FIBER TENSION (P) mg
-ln(S)

FIG. 11

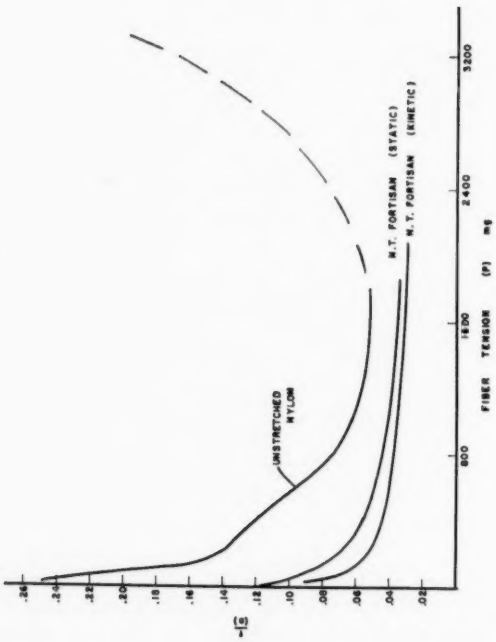

FIG. 8

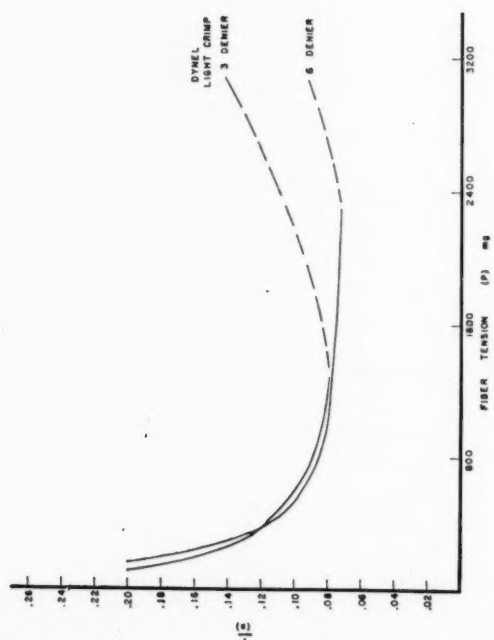

FIG. 10

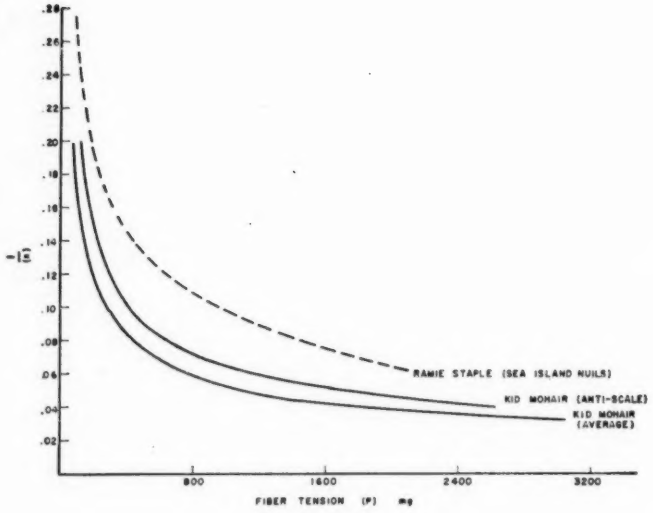

FIG. 12

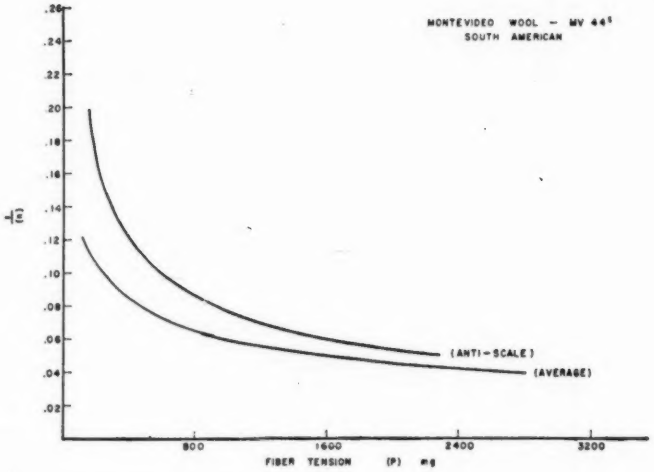

FIG. 13

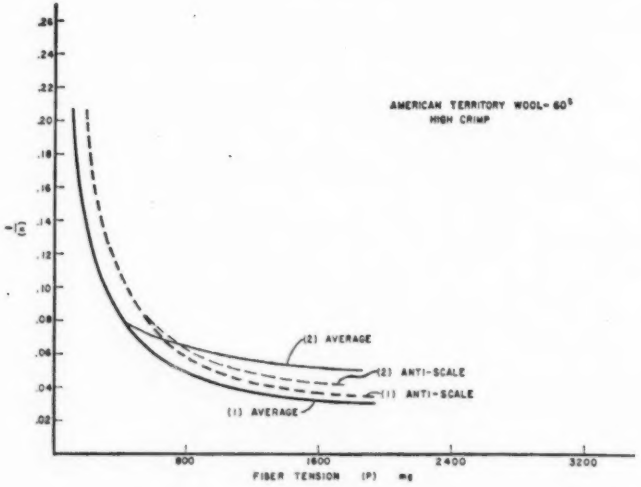

FIG. 14

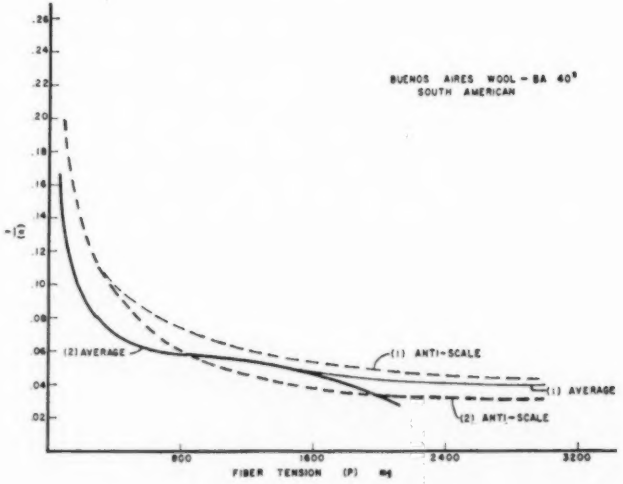

FIG. 15

distinct twists about its longitudinal axis, with helix frequently reversed. The twists are commonly known as spirals or convolutions. The contact between cotton fibers, even in a highly twisted cotton strand, is intermittent, with contact occurring at the tips of the convolutions; however, Adderley [1] presented evidence that there is also an interlocking of the convolutions which can be seen under the microscope, but the number of fiber contacts is few even at high normal pressure. Thus, the number of convolutions, the regularity of convolutions, the ratio of convolution between fibers, and the reversals of the convolutions may all have an effect on the clinging power of the cotton.

Although the present machine is very adaptable to this type of study, time limitations prevented an investigation of the effect of these factors. Little investigation was made of the effect of temperature and humidity on the clinging power, although a decrease in clinging power was observed for an increase in humidity. The crimp and the number of convolutions per inch vary with the moisture content of the fiber, which may possibly be the cause. The effect of wax content, fiber maturity, and mercerizing was not investigated, but the author feels that they probably all have an effect on clinging power. Recoving the wax from the fiber would probably increase the clinging power, since it would expose the fibrillar cellulose skeleton. Mercerizing cotton fibers swells them to a more cylindrical shape, and thus probably reduces the clinging power, which is dependent on such structural effects as convolutions; this also results in a stronger yarn due to closer packing of the fibers and more fiber contacts.

Balls [2] in his study of quality in cotton said that the fibers should be slippery during drafting, but that a high friction is desired in spinning. High fiber friction naturally increases the strength of the finished yarn, but much work has yet to be done before the relationship between the frictional characteristics of fibers and the resulting drafting and spinning properties are fully understood. It is possible that the shape of the frictional characteristic curve of a particular fiber may be definitely correlated with the behavior of the fibers during drafting. In other words, the behavior of the fibers during drafting or spinning may be more dependent on the relationship between the values of the friction of a particular fiber at different stresses than on the value of the friction at any particular stress.

An investigation of the effect of the relative speed at which the fibers are rubbed was made, and it was found that at higher speeds the fibers chattered, although no change in the friction was observed. No investigation of this effect was made on fibers other than cotton. A speed was chosen just low enough to prevent chatter between cotton fibers, and was used for all the fibers tested. It is also important that the speed be low enough so that fiber behavior can be observed easily.

The effect of colloidal silica dispersions on the clinging power of cotton was observed (see Figure 7). Clinging power increased upon the application of silica, and was greater as the normal pressure increased. This is as expected, since at higher normal pressure more fiber contacts occur at which the silica can take effect. Continued rubbing of the fibers treated with silica caused a slight increase in the friction observed at high values of normal pressure. Abrasion of the silica particle deposited on the fiber by the colloidal silica probably caused the agglomerates to break up into smaller particles, which were in turn distributed along the fibers, causing a more uniform distribution of the silica and thus a greater friction. Continued rubbing of fibers without silica caused a slight decrease in the friction observed. Other investigators have observed a decrease in friction between fibers with an increase in temperature; it is therefore possible that the decrease in friction observed is due to a localized increase in temperature between the fibers due to abrasion. There was less variance between fiber pairs treated with colloidal silica than between untreated pairs, which indicates that the friction of silica-treated fibers is under better control than that of untreated fibers. In all cases the presence of silica caused a marked flattening of the friction-stress curve; or, in effect, the percentage change of drag for a given change in fiber stress was much less when the total drag had been increased by the presence of colloidal silica.

Nylon

Unstretched filament nylon was tested, and the resulting curve is shown in Figure 8. Little variance was found between fiber pairs tested in comparison with the other fibers tested. This would be expected since nylon fibers have a fairly uniform circular cross section, which is not characteristic of the other fibers tested. Vibration, or chatter, was

present during fiber slippage. The vibration seemed to decrease in amplitude as P increased, but increase in frequency until P reached a value of about 1800 mg., at which time the fibers stuck together fast and severe tapping of the fibers would not cause the fiber to slip. Increasing P beyond this point caused the fibers to stick together at a decreasing value of n for increasing P. This same sticking effect was also observed for cuprammonium rayon (Figure 9) and Dynel (Figure 10), but no chatter was present with the cuprammonium rayon. No permanent elongation of the nylon was observed for the values of P observed. It is possible that the chatter was due to the particular velocity at which the fibers were rubbed, and may not be present at a different velocity. The effect of velocity was not investigated, and thus deserves further study.

Fortisan

A distinct difference between static and kinetic friction was found for Fortisan. Both values were observed, and are given in Figure 8. A high-amplitude vibration was observed, but no cementing action. This fiber was more slippery than any of the other fibers tested.

Ramie

Ramie has a very irregular surface structure, which probably accounts for the high friction observed (see Figures 6 and 12), but the results seem to contradict the general belief that the difficulty of processing ramie fibers is due to the slippery nature of the fibers.

Viscose Rayons

Italian Snia, Purlino, and Tovis viscose rayons were tested, and the results are shown in Figure 11. The Tovis rayon was very fine and had a high crimp, which disappeared when P reached 100 mg. and thus had little effect. The others had no crimp, but did have slight wrinkles at values of P less than 100 mg. The Tovis viscose has very low friction and a crenulated cross section, and should be compared with the Italian Snia viscose, which has a high friction and an E-shaped cross section. At higher values of P all three showed a decrease in friction due to continuous rubbing. This may be due to an increase in temperature due to abrasion or to the stress-strain properties of the fibers. A decrease in friction was observed upon retesting a pair of fibers after the fibers had been elongated by stretching. As with many of the other more elastic fibers, care must be taken when approaching the critical value of n where fiber slippage stops that the fibers are actually slipping and that one is not just observing stretching and recovery of the fibers at one end of the twisted structure.

Wool and Mohair

The curves found for wool and mohair are given in Figures 12–15. Values were obtained for both the anti-scale friction and "average" friction. The anti-scale friction was observed by mounting one fiber with its tip end upward and the other with its tip end downward, and then observing n when the fiber slip was in the anti-scale direction. The average friction value was obtained by mounting both fibers with their tip ends either up or down, where the fiber slips tip end to root end. The average value was obtained because it was found difficult to observe the with-scale friction. As was expected, the anti-scale friction was found to be greater than the average friction. We would expect the average friction to be greater than the with-scale friction if the latter were observed. A definite catching action was observed when the fibers stopped slipping in the anti-scale direction, while no such action was apparent when observing average friction values. The fine crimp present with the territory wool can be neglected when P reaches 600 mg.

There are several observations which should be made from an inspection of the resulting curves. First, it will be observed that the slopes of the curves are quite steep at high values of P. It would appear at first that μ is dependent on the normal pressure to a great extent, but it is possible that it is partly due to some sort of scale action. The best explanation would seem to be that the scales cause the coefficient of friction to depend on the apparent area of contact and to increase with an increase in the apparent area of contact. Lindberg and Gralén [3] observed the same effect and indicated that such a relationship between the coefficient of friction and the apparent area of contact was the best explanation. They considered the anti-scale friction as being composed of two parts: one part being the same as the with-scale friction, and dependent on the normal pressure like other fibers, and the other part

being due to the scales, which is also dependent on the normal pressure. At very low normal pressures, few scales will contact each other because the scales are of various heights and will not always coincide with one another on the two fibers. At higher normal pressure, the friction due to the scales will increase, but will reach a limit when the maximum possible number of scales come into contact. Likewise, if the apparent area of contact is increased, the resistance due to the scales is proportionally increased. Since for a constant area of contact the resistance due to scales reaches a maximum, the difference between the friction with scales and without scales would be inversely proportional to the normal force and after the maximum is reached would decrease with an increase in normal pressure. Thus, by this theory it can be concluded that the over-all coefficient of friction increases with an increase in the apparent area of contact and also increases with the normal pressure at an even faster rate than when the scales are not present, until the maximum scale resistance is met. The results found are in excellent agreement with this theory. Lindberg and Gralén considered this theory in the light of the ratchet theory, which is reputed by most authors, but it is not necessary that the ratchet theory be valid because just a difference in the angle of contact of the scales in the with-scale and anti-scale direction will cause the same scale action. Inspection of Figures 14 and 15 will disclose two types of fiber behavior for these fibers, indicated by the curves marked (*1*) and (*2*). Fibers behaving as (*1*) give curves similar to those found for kid mohair and American territory wool, but fibers behaving as (*2*) are unexplainable. It will be observed that the average friction value behaves as before until a critical value of P is reached, at which time the average friction curve crosses the anti-scale curve, giving a higher friction to the average value. Explanation for this phenomenon cannot be given, unless possibly it is connected with the stress-strain relationships of the fibers or is due to deformation of the scales by stress concentration. However, it should be stressed that it was only observed for the average value and not for the anti-scale friction. Also, no decrease in the friction in the anti-scale direction was observed after continuous rubbing of the fibers. This is certainly a phenomenon which deserves further study.

Conclusions

1. A means for investigating interfiber friction has been developed. The resulting instrument is based on the fiber twist principle; its usefulness as a tool of investigation in the study of interfiber friction has been shown. Its main virtues are its broad adaptability and simplicity and its realistic consideration of the nature of interfiber contact in textile materials.

2. The presence of fiber crimp was found to increase greatly the frictional resistance of the fibers.

3. Evidence was found that the coefficient of friction may be dependent on both the real and apparent areas of contact for wool, and hair fibers possessing some form of scales, and cotton.

4. Colloidal silica dispersions were found to increase greatly the clinging power of cotton, and to give better control over cotton fiber friction.

5. It was shown that the shape of the frictional characteristic curve of a particular fiber may be definitely correlated with its behavior during drafting—that is, the behavior of the fibers during drafting or spinning may be more dependent on the relationship between the values of the friction of a particular fiber at different stresses than on the value of the friction at any particular stress.

Recommendations for Future Investigations

1. The friction between two single fibers of different types should be investigated to give insight into the interfiber friction in the blending of textile fibers.

2. A study of the effect of the number of convolutions, the uniformity of convolution, the maturity, the wax content, and mercerizing on the clinging power of cotton should be made.

3. Further study must be given to the effect of colloidal silica and other roughing agents on the clinging power of cotton.

4. Correlation should be made between the frictional nature of fibers tested and the drafting and spinning properties of these fibers.

5. The nature of interfiber contact should be studied by observing the slippage of fibers in the machine under the microscope.

6. Further investigation must be made of the effect of velocity and helix angle on fiber friction.

7. The effect of the stress-strain properties of a particular fiber on the friction of that fiber should be investigated.

8. The machine should be used to study the abrasion properties of textile fibers.

9. Further fiber testing should be done on a completely statistical basis, to which the frictional testing device developed is particularly adaptable.

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A Single-Fiber Load-Elongation Tester for Cotton*

Rollin S. Orr and James N. Grant

Southern Regional Research Laboratory,† New Orleans, Louisiana

Abstract

A single-fiber tester of the type employing a constant rate of loading is described. Designed especially for obtaining load-elongation curves in addition to end-point data on cotton fibers, it employs coiled-spring loading and optical means of recording. Devices are incorporated that permit cyclic loading studies and static life determinations. An oven and humidification tank are provided for testing at various temperatures and under various moisture conditions.

STUDIES of the physical properties of single fibers taken from treated fabrics aid in the analysis of effects of such treatments on fabric properties and performance. Owing to the extreme variability of cotton fibers and the large number of tests that must be made, the tester used in such investigations should be simple to operate and adjust, and must give results rapidly and accurately.

Studies at the Southern Regional Research Laboratory of breaking load and elongation at break of single cotton fibers have been reported [10, 15]. The tester used in those investigations, while it met the above requirements, gave only the end-point determinations.

The tester described here, which is also accurate and simple to operate and adjust, gives load-elongation and cyclic loading curves of single cotton fibers under various temperature and moisture conditions, as well as end-point determinations. This tester was developed because there was then none on the market suitable for use in such studies.

Types of Testers

The two general types of testers described in the literature were considered for use in studies of single fiber properties.

In the first type, tension results from the displacement of a weight connected to the fiber. Examples are the pendulum testers of Balls [2], Gonsalves [8], and the German testers [19], and the chainomatic loading testers of de Meulemeester [7] and Sookne and Rutherford [21]. Testers of the pendulum type are slow and tedious to operate since even slight movements of the weight attached to the fiber may cause relatively large inertia forces to be set up in such instruments, and extreme care is required in attaching the fiber. Also, a slow rate of loading is necessary to avoid vibration of the weight.

In the second general type of tester, tension is applied to the fiber by deforming an elastic mem-

* The principle and construction of this instrument were discussed very briefly in a paper presented before The Fiber Society, Fontana, N. C., Apr. 27, 1950.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

ber. Testers of this type may be classified into two groups. In one group, illustrated by the testers of Polanyi [17], Steinberger [22], Lonsdale [13], Sikorski [20], and Asmussen [1], the movement of the elastic member is slight compared to the elongation of the fiber. This slight movement is magnified by optical or electrical means. Elongation of the fiber is measured directly from the distance traveled by a clamp opposite the elastic member. Most electric strain-gage instruments can be classified in this group [3, 6, 18].

In the other group of this second type of tester, the movement of the elastic member is great in comparison to the elongation of the fiber. The testers of Chevenard and Champetier [4] and Cliff [5] illustrate this type. The latter instrument was used extensively by Meredith [14]. The deformation of the elastic member is large enough to serve as a measure of force without magnification, and only a small correction due to the elongation of the fiber is required. Fiber elongation is measured with a measuring microscope or optical lever system which magnifies the movement of the fiber end clamped to the elastic member. Since slight movements in the elastic member produce only small changes in the tensional force on the fiber, testers of this group are less sensitive to small external vibrations in the equipment than the pendulum type testers. They can be operated at faster rates of loading, and the operation of clamping the fibers without damage can be speeded up. In the design of the instrument described below the principle of testers of the last group was used. The arrangement of parts, the values of the spring constant, and the design of the optical system were adapted to meet the requirements for testing cotton fibers.

Description and Operation

General Design

The single-fiber tester is illustrated in Figure 1. It consists essentially of a load-elongation mechanism, *A*, a temperature control oven, *B*, and a humidification tank, *C*.

Figure 2 is a schematic diagram of the load-elongation mechanism. The fiber is held between the clamps, *E* and *F*. Tension is applied to the fiber by elongation of a coiled steel spring, *B*, attached to the upper clamp, *E*. The spring is elongated with a

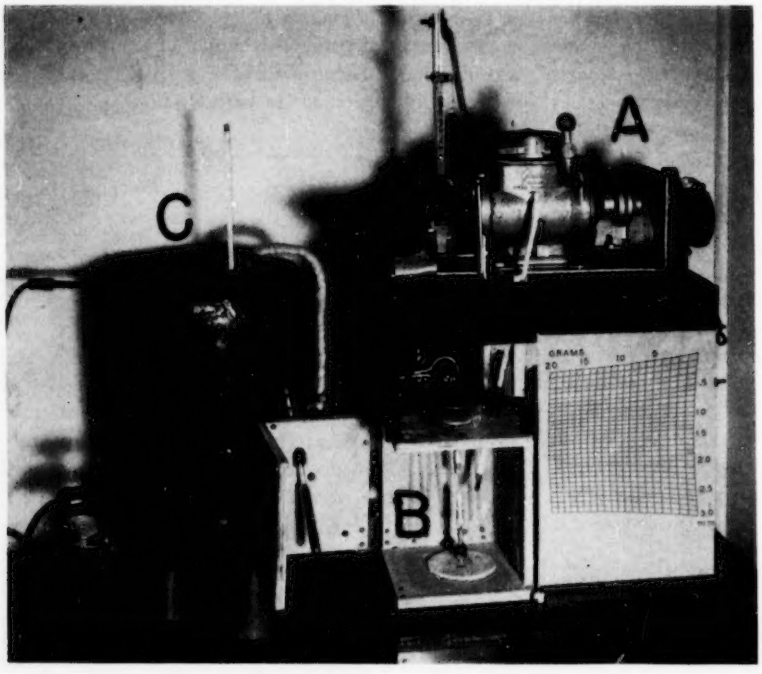

FIG. 1. *Photograph of single-fiber tester.*

ladder chain, *H*, which is driven by the motor through a variable speed unit, *D*.

Elongation of the fiber is magnified about 50 times by an optical lever system. Light from the lamp, *A*, illuminates the pinhole, *P*, an image of which is brought to a focus by a lens, *L*, as a small illuminated spot about $\frac{1}{2}$ mm. in diameter on the screen, *S*, by reflection from optical lever mirrors, *m* and *M*. Elongation of the fiber rotates optical lever *m* about the horizontal axis, *N*, to cause the vertical movement of a spot of light on the screen, *S*. The optical lever is supported on a pin bearing, *N*, and attached to the upper clamp, *E*, by a small ball and socket joint. Load is registered horizontally on the screen by rotation of the long mirror, *M*, about a vertical axis which is geared to the motor. The angular rotation of the long mirror is proportional to the elongation of the coiled spring. Thus, the spot of light traces a load-elongation curve on the screen. Breaking load may be read directly from the counter, *C*, which is so geared to the ladder chain as to read directly in grams when a spring with a 1.0 g./cm. spring constant is used.

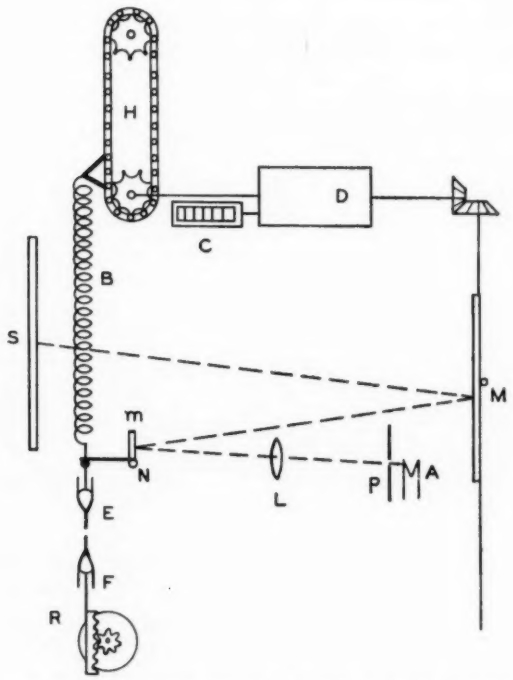

FIG. 2. *Schematic diagram of load-elongation mechanism of the single-fiber tester.* E *and* F—*Fiber clamps.* B—*Coiled steel spring.* H—*Ladder chain.* D—*Motor and gear drive.* C—*Counter.* A—*Light source.* P—*Pinhole.* L—*Lens.* m—*Optical lever mirror.* M—*Mirror geared to motor.* N—*Pin bearing.* S—*Load-elongation screen.* R—*Rack and pinion.*

Electrical Circuit

In Figure 3 is given the electrical circuit with switch contacts in the position for clamping the fiber. A hand-operated control switch, *C*, is located in a position easily accessible to the operator. When a fiber breaks, a sensitive switch, *S*, which normally is closed to the motor, is thrown by the movement of the upper jaw to stop the reversible motor, *D*, and to actuate a brake, *B*, which prevents overcoast of the counter. Upper and lower limit switches, *U* and *L*, are opened by lugs attached to the ladder chain. Switches *C*, *S*, and *U* are single-pole, double-throw, snap-action switches; *L* is a single-pole, single-throw, snap-action switch. A timer, *T*, is used to obtain the static life of a fiber under a load determined by setting of the upper limit switch. A lamp, *A*, illuminates the pinhole, *P* (Figure 2). Cyclic loading curves between zero and a fixed load are obtained by placing control switch *C* where it will be reversed by a lug on the ladder chain. Other cyclic loadings are done manually.

Temperature and Humidity Controls

While atmospheric conditions during the test are usually those standard for textile testing, it is often desirable to evaluate the elastic properties of the fibers at atmospheric conditions encountered in service. The oven (Figure 1, *B*) is equipped with an electric heater controlled with a mercury thermo-

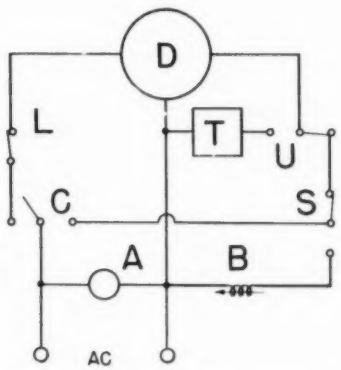

FIG. 3. *Diagram of electrical circuit of tester.*

regulator. The humidity is controlled by bubbling air under 4 oz. of pressure through an insulated tank (Figure 1, *C*) containing water at the desired dew point temperature. The saturated air is heated above the dew point by electrically heated pipes which carry the air into the oven under a slight pressure to increase circulation. A rate of flow of about 0.5 cu. ft./min. rapidly restores the conditions changed by opening the oven to mount specimens.

Calibration of Tester

The tester is calibrated for load-elongation measurements with standard weights gripped in the upper jaw (Figure 2, *E*). Paper is placed over the screen, *S*, and the path of the spot of light is traced as the upper jaw is slowly raised. Weights are added in units of 1 g. for successive traces. The elongation axis is calibrated by gripping stiff paper in the jaws and tracing the path of the spot of light as the spring is elongated. This is repeated with each 0.1 mm. advancement of the jaws. The jaws are moved with the rack and pinion (Figure 2, *R*). The jaw position is checked with a measuring microscope. The calibration chart (shown on the instrument, Figure 1) is thus constructed. The departure from orthogonal coordinates is due to the variation in magnification of the optical levers over the areas of the chart.

Mounting Fibers

The single fiber is attached to the opposite sides of a U-shaped fiber mount, as described in previous publications [12, 15].

Tension is often developed in fibers due to warp of paper mounts when the cement dries. The resulting fiber breakage and lowered elongation have been reduced by the use of aluminum foil. The foil is roughened with fine sandpaper to increase adhesion of the cement. A cement that would be usable over the wide range in temperatures and moisture conditions needed in the testing of fibers, without either some slippage or breaking due to strains at the cement fiber junction, was not found. One consisting of a slow-drying solution of polystyrene proved satisfactory for testing at standard conditions, where slippage of 0.03 mm. is obtained on fibers of 7 mm. specimen length. Cellulose acetate was used for temperatures above 100°C.

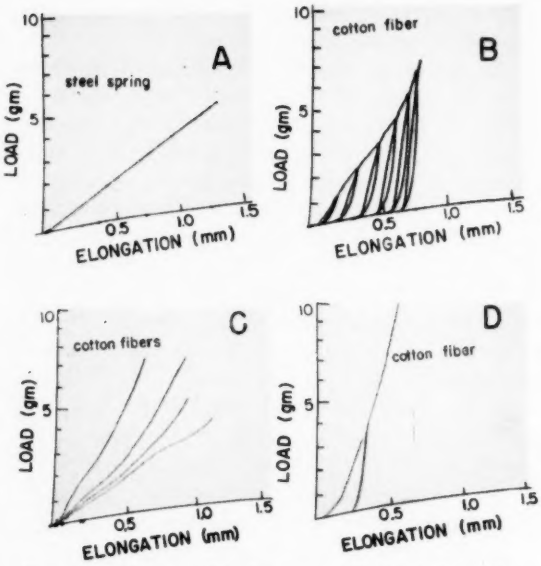

FIG. 4. *Photographically recorded load-elongation curves.*

Testing Procedure

After the fiber is attached and the cement has hardened, the lower section of the U is cut off of the mount, leaving the fiber of known specimen length attached to the tabs. The tabs are placed in the clamps (Figure 2, *E* and *F*), and a small initial load (0.2 g.) is applied to remove most of the natural curls before beginning the record. The spot of light is adjusted to read zero elongation by movement of the lower clamp. The specimen length is accurately determined at this time with a measuring microscope. Length is measured on only ten of each 100 specimens, since the variation in specimen length is small. Measurements to determine slippage in the glue are also made on these fibers.

A record of the movement of the spot of light across the screen is usually made by tracing the spot with a pencil on translucent drawing paper. It can be made by placing photographic paper against the screen, but the photographic process is used only at high rates of loading. If only breaking load and elongation at break are desired, the elongation can be followed visually by movement of the spot of light on a graduated scale and the reading noted when the specimen fails. Breaking load is then read from the counter (Figure 2, *C*), but must be corrected for elongation of the fiber. Since the spring con-

stant is about 1.0 g./cm. extension, the correction for cotton fibers tested at ¼ in. specimen length is about 0.05 g. This correction is made in average breaking load; however, it is considered negligible in the calculation of variance.

Load-Elongation Curves

Typical Curves

Figure 4 shows typical load-elongation curves which represent the trace of the spot of light recorded on bromide paper. Curve *A* is the trace of the spot when a steel spring was placed between the fiber clamps. The spring was loaded to 5 g. and unloaded to zero load to give the loading and unloading curves. The traces were so nearly the same that the differences were unobservable. Curve *B* is the trace of the spot when a cotton fiber was loaded and unloaded. The loads were increased in units of 1 g. for each cycle. The plastic flow and hysteresis loops of the material are evident from the curve. Curves *C* are the load-elongation curves of four fibers of the same length from a sample of Rowden cotton, illustrating the differences in elastic properties of individual fibers from the same cotton. Curve *D* shows the load-elongation curve of a fiber which was loaded to 3 g., and then subjected to nine unrecorded cycles of repeated unloading and loading, followed by the recorded tenth cycle.

Use of Curves

Load-elongation curves can be obtained with the instrument at the rate of 50 fibers an hour. This rapid rate of testing means that the number of tests needed for reliability can be made within a length of time considered practical for fundamental studies. The precision for measurements of strength and elongation at break for 300 fibers is about 4% within the 90% confidence interval.

Load-elongation curves obtained with this single-fiber tester have been useful at the Southern Regional Research Laboratory in investigations of the changes in elastic properties of cotton fibers as a result of mechanical processing [11], chemical modification [9], and heat degradation [16]. Such curves are essential in fundamental studies of the mechanical properties of textile fibers.

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Effect of a Wetting Agent on the Hydrolysis of Highly Methylated Cotton Cellulose

Richard E. Reeves and Bernard J. Barrett

Southern Regional Research Laboratory, New Orleans, Louisiana*

Abstract

The acid-catalyzed, heterogeneous hydrolysis of a highly methylated cotton cellulose has been investigated, with particular attention to the effect of incorporating a wetting agent in the hydrolysis medium. It was found that the amount of fast-reacting material was small when the aqueous acid did not contain a wetting agent, but was increased severalfold in the presence of an active wetting agent. The rate constant for the slow-reacting material was also increased by the wetting agent. The minimum viscosity reached during hydrolysis was the same in the presence or in the absence of the wetting agent.

IN STUDIES on the heterogeneous hydrolysis of highly methylated cotton cellulose, Reeves, Barrett, and Mazzeno [3] observed that the intrinsic viscosity (in chloroform) of the material not dissolved by the hydrolysis medium decreases sharply, passes through a minimum, and then increases upon prolonged hydrolysis. Different minimum values were obtained for each of five batches of methylated cotton cellulose prepared from the same purified cotton. The values ranged from 0.37 to 0.58 dl./g. and varied with the manner of preparation of the methyl cellulose.

Steele and Pacsu [4] hydrolyzed a sample of highly methylated cotton cellulose to an intrinsic viscosity of 0.64 dl./g. They calculated that this viscosity represented an average degree of polymerization of about 60 glucose units, pointing out that their results supported the theory of Pacsu [2], which requires the occurrence of regularly spaced weak linkages in cellulose at about every 64 glucose units. But the fact that minimum viscosity is influenced by the method of methylation [3] precludes the use of viscometrically determined degrees of polymerization as a measure of the distance between weak linkages existing in the cellulose before methylation.

The downward trend exhibited even in the most extensively hydrolyzed samples reported by Steele and Pacsu [4] suggested that they may have been mistaken in assuming that a limiting viscosity had been reached in their work. To investigate this possibility, a sample of highly methylated cotton cellulose was hydrolyzed under the same conditions that they had employed, but for longer periods of time. The viscosity continued to decrease long after the time when Steele and Pacsu had terminated their hydrolyses.

Comparison of our results using Steele and Pacsu's conditions (no wetting agent) with our previous results [3] (with a wetting agent) led to the discovery that the course of hydrolysis of highly methylated cellulose is markedly affected by the presence of a wetting agent.

Experimental

The highly methylated cotton celulose was that described and designated as batch *E* in the previous publication [3]. This batch had the lowest minimum viscosity and the least pronounced viscosity increase upon prolonged hydrolysis of any of the five batches investigated. It contained 44.5% methoxyl.

Hydrolyses were conducted with *N*-hydrochloric acid in flasks immersed in a water bath regulated to 60° or 80° ± 0.1°C, and without a wetting agent, as described by Steele and Pacsu [4]. For comparison, some additional experiments were made with the wetting agent Aerosol OS.* All samples were

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

* The mention of a trade product does not imply its endorsement by the Department of Agriculture over similar products not named. Aerosol OS is stated by the manufacturer to be isopropyl naphthylsulfonate.

TABLE I. THE HYDROLYSIS OF METHYL CELLULOSE WITH *N* HCl AT 80°C

Hours	No wetting agent		Aerosol OS, 0.10 g./100 ml.*	
	Residue (%)	Intrinsic viscosity in $CHCl_3$ (dl./g.)	Residue (%)	Intrinsic viscosity in $CHCl_3$ (dl./g.)
1	—	5.8	—	1.32
4	97.4†	—	96.3	.83
8	94.7	2.16	93.7	.54
24	93.4	.98	85.2	.40
48	—	—	75.4	.38
73	—	—	71.6	—
96	83.1	.49	68.6	.37
144	77.6	.41	59.8	.37
288	61.6	.37	45.8	.38
380	55.7	.37	—	—

* These data were presented in graphical form in [3].

† Identical values were obtained with duplicate samples, one of which was shaken only at the start of the hydrolysis period and the other shaken continuously during the hydrolysis period.

shaken vigorously with the aqueous acid for several seconds immediately after mixing and only intermittently thereafter, except for one set of duplicate samples. To investigate the possible influence of shaking upon the rate of hydrolysis, one sample was shaken only at the start of the hydrolysis period, while a duplicate sample was shaken throughout; these samples were hydrolyzed for 4 hrs. at 80°C without wetting agent.

After hydrolysis the undissolved residues were filtered on sintered glass disc crucibles, washed free of acid with hot distilled water, and allowed to dry in air. They were then weighed, and viscosity determinations were made on most of the samples.

Viscosity measurements were made at 25°C with the samples dissolved in redistilled chloroform. Three different concentrations were employed for each sample, and intrinsic viscosities were computed by linear extrapolation to zero concentration of the function η_{sp}/C *versus* concentration, C. Each chloroform solution was passed through a sintered glass disc before determination of its viscosity, but the amount of material retained on the disc amounted to less than 1% for most of the hydrolyzed specimens.

Although Gibbons [1] presented data which indicates that a portion of the ether-linked methoxyl is removed during the drastic *homogeneous* hydrolysis of methyl cellulose, it has been observed [4] and confirmed [3] that no appreciable amount of ether-linked methoxyl is removed from the insoluble phase during *heterogeneous* hydrolysis under the conditions employed in the present experiments.

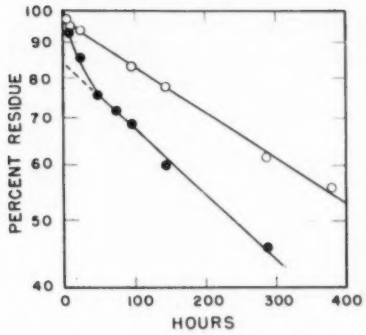

FIG. 1. *The percent residue remaining during the hydrolysis of methyl cellulose with N HCl at 80°C.* Upper curve—*Without a wetting agent.* Lower curve—*With 0.10 g. Aerosol OS per 100 ml.*

Results and Discussion

Table I records percentage residues and intrinsic viscosities after hydrolysis for various periods of time at 80°C with and without the wetting agent. It is apparent that the decrease in viscosity in the early stage of hydrolysis occurred much more rapidly in the presence of the wetting agent. Graphical representation of the data in Table I indicated that in order to reach an intrinsic viscosity of 1, only 2.5 hrs. were required with a wetting agent while 23.5 hrs. were required without. The minimum viscosity was first observed after 96 hrs. of hydrolysis with a wetting agent, while the same viscosity was observed after 288 hrs. of hydrolysis without a wetting agent. The lower limit for the viscosity was the same with or without the wetting agent. These experiments leave unanswered the question of whether prolonged hydrolysis without the wetting agent would have produced an increase in viscosity above the minimum value such as was observed upon prolonged hydrolysis with the wetting agent [3].

In Figure 1 are plotted the percentage residues on a log scale *versus* the duration of hydrolysis at 80°C. The figure clearly shows that the amount of fast-reacting material and the rate of hydrolysis of the slow-reacting material are both markedly increased by the wetting agent. Apparent first-order constants calculated for the slow-reacting material from the straight-line portions of the curves of this figure were 2.08×10^{-3} hrs.$^{-1}$ with wetting agent

TABLE II. THE INTRINSIC VISCOSITY CHANGES UPON HYDROLYSIS OF METHYL CELLULOSE WITH *N* HCl AT 60°C

Hours	Intrinsic viscosity in $CHCl_3$	
	No wetting agent	Aerosol OS, 0.10 g./100 ml.
	(dl./g.)	(dl./g.)
8	—	4.45
24	2.8	1.3
96	1.2	.59
267	—	.42
288	.66	—
576	.48	.38
1152	.40	.37

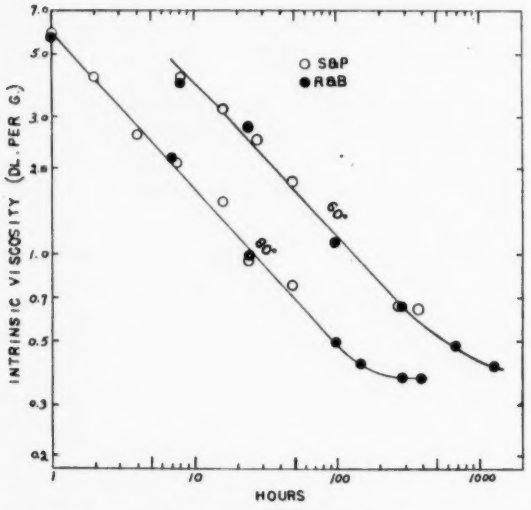

FIG. 2. *A comparison of intrinsic viscosities reported by Steele and Pacsu [4] with those observed in this work during the hydrolysis of methyl cellulose with* N *HCl in the absence of a wetting agent.*

and 1.47×10^{-3} hrs.$^{-1}$ without. The intercepts at zero time, made by extrapolating to the ordinate the straight-line portions of the curves, indicate that the amount of fast-reacting material increased from 4% without a wetting agent to 17% with the wetting agent. No difference attributable to the amount of shaking was noted (Table I).

Table II records intrinsic viscosities after hydrolysis for various periods of time at 60°C with and without the wetting agent. Again the viscosity decreased much faster in the presence of the wetting agent. These data, like those recorded by Steele and Pacsu [4], are not sufficient to establish either a minimum or a limiting viscosity because they do not show an end to the downward trend. However, it is apparent that without a wetting agent the minimum value was not reached even after 1,152 hrs. of hydrolysis.

Since the most drastic hydrolyses reported by Steele and Pacsu were 46.9 hrs. at 80°C and 366.3 hrs. at 60°C, both without wetting agent, it seems reasonable to conclude that these workers did not observe the minimum viscosity obtainable with their methyl cellulose. This conclusion gains considerable support from the graphical presentation of the comparable data, as shown by Figure 2. In this figure intrinsic viscosity is plotted against the time of hydrolysis, both on a log scale. It is apparent that there is excellent agreement between the data obtained in the present investigation and that reported by Steele and Pacsu down to the point where the latter workers discontinued their hydrolyses.

Summary

The rate of hydrolysis of highly methylated cotton cellulose is markedly increased by the addition of a suitable wetting agent. The wetting agent employed in these experiments gave a fourfold increase in the proportion of highly reactive or "accessible" material. It also increased the rate of reaction during the second stage, the hydrolysis of the slow-reacting material. The wetting agent did not alter the minimum viscosity of the undissolved residue (in chloroform), but it greatly shortened the time of hydrolysis necessary to arrive at the minimum value.

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(*Manuscript received November 3, 1952.*)

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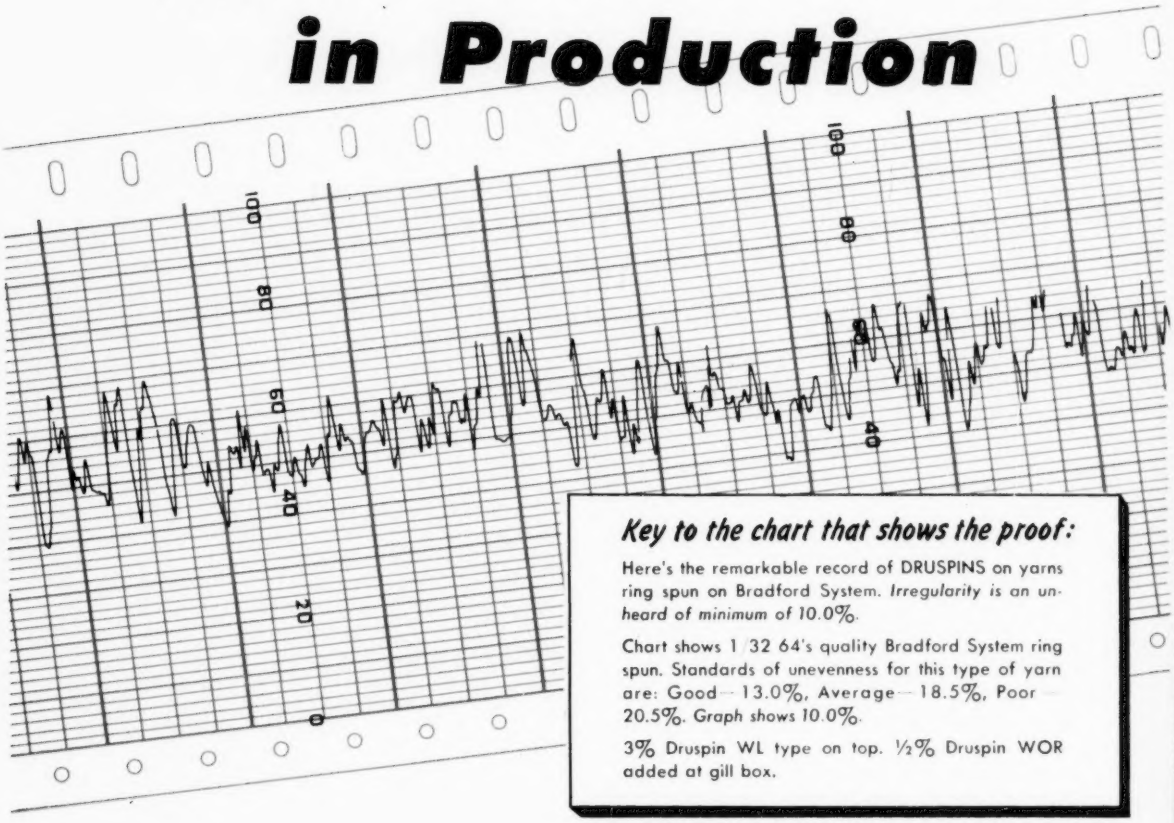

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